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(54) IONIC SILICONE HYDROGELS

IONISCHE SILIKONHYDROGELE

HYDROGELS À BASE DE SILICONE IONIQUE

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Description

Related Applications

[0001] This application claims priority to U.S. Patent Application No. 13/720,286 filed on December 19, 2012 entitled IONIC SILICONE HYDROGELS; and U.S. Provisional Patent Application No. 61/579693, filed on December 23, 2011 entitled SILICONE HYDROGELS COMPRISING N-VINYL AMIDES AND HYDROXYALKYL (METH)ACRYLATES OR (METH)ACRYLAMIDES, and U.S. Provisional Patent Application No. 61/579683, filed on December 23, 2011 entitled SILICONE HYDROGELS HAVING A STRUCTURE FORMED VIA CONTROLLED REACTION KINETICS.

Field of the Invention

[0002] The present invention relates to ionic silicone hydrogels having an exceptional balance of properties which are generated by controlling the reaction kinetics of the components of the reaction mixture.

Background of the Invention

[0003] Soft contact lenses made from silicone hydrogels offer improved oxygen permeability as compared to soft lenses made from non-silicone materials such as poly(2-hydroxyethyl methacrylate) (HEMA). Initial efforts to make silicone hydrogel contact lenses were hampered by the poor wettability, high modulus, poor clarity, hydrolytic instability or the high cost of raw materials used to make many of these silicone hydrogels. While various solutions have proven somewhat successful for each of these deficiencies, there remains a need for silicone hydrogels that can be made from inexpensive commercially available monomers, and which have excellent wettability (without the need for surface modification), low modulus, good clarity, and desirable oxygen permeability.

[0004] Silicone hydrogels formulations containing polymeric wetting agents, such as poly(N-vinylpyrrolidone) (PVP) and acyclic polyamides have been disclosed. However, these polymers are quite large and require the use of special compatibilizing components, which need to be custom manufactured. Examples of compatibilizing components include 2-propenoic acid, 2-methyl-,2-hydroxy-3-[3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propoxy]propyl ester (SiGMA).

[0005] An alternative means of forming a wettable silicone hydrogel lens is to incorporate monomeric N-vinylpyrrolidone (NVP) into the monomer mix used to make the silicone hydrogel polymer, typically in amounts of about 25-55% (by weight) of the monomer mix. Such materials have been described in US patents 4,136,250; 4,153,641; 4,260,725 and 6,867,245. The materials described in these references generally incorporate polyfunctional silicone monomers or macromers, that act as crosslinking agents, and thereby increase the modulus of the final polymer. US 4,139,513 discloses that 2-propenoic acid, 2-methyl-,2-hydroxy-3-[3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propoxy]propyl ester (SiGMA) can be used to form lenses from formulations comprising NVP and HEMA. SiGMA is the only source of silicone disclosed. However, because of the relatively low silicone content in those monomers, desirable levels of oxygen permeability in the final polymers are difficult to achieve.

[0006] US 2010/0048847 discloses silicone hydrogels made from a blend of a monomethacryloxyalkyl polydimethylsiloxane methacrylate with about 52% NVP, HEMA and TRIS, and using a blend of ethanol and ethyl acetate as a diluent. The polymers disclosed are (to varying degrees) hazy, but it was disclosed in this application that the haziness could be reduced by the addition of at least about 1.5 % methacrylic acid (MAA).

[0007] Addition of anionic monomers such as MAA can, however, cause hydrolytic instability in silicone hydrogels, as was disclosed in "The role of ionic hydrophilic monomers in silicone hydrogels for contact lens application", Lai, Y., Valint, P., and Friends, G.; 213th ACS National Meeting, San Francisco, April 13-17, 1997. For this reason, it remains desirable to form clear, hydrolytically stable, wettable (without surface treatment) silicone hydrogels with low moduli from a combination of a monomethacryloxyalkyl polydimethylsiloxane methacrylate such as mPDMS, and NVP.

[0008] US2010249356 (A1) relates to a polymer formed from reactive components comprising at least one silicone component and at least one ionic component comprising at least one anionic group.

[0009] US2002107324 (A1) describes a soft contact lens containing a silicone-hydrogel made by curing a reaction mixture containing a silicone-containing monomer.

[0010] US2011230589 (A1) provides transparent silicone hydrogels obtained by polymerizing a monomer mix containing a plurality of monomers, wherein the monomer mix comprises about 30 to about 98% by weight of at least one type of silicone monomer which is, and about 1 to about 50% by weight of at least one type of non-silicone type (meth)acrylamide monomer containing two or more hydroxyl groups within a molecule; wherein the weight percents are based upon the total amount of monomer components and polymer components in the monomer mix.

Summary of the Invention

[0011] The present invention is defined by the claims.

[0012] The silicone hydrogels of the present invention are useful for making biomedical devices, ophthalmic devices, and particularly contact lenses.

Description of the Figures

[0013]

Figure 1 is a schematic of a lens assembly.
Figure 2 is a schematic of the dual compartment cure box used for the kinetic evaluations.
Figure 3 is a schematic of compartment 2 of the cure box show in Figure 2

Detailed Description of the Invention

[0014] The present invention relates to ionic silicone hydrogels formed from reaction mixtures comprising at least one hydrophilic component and anionic component which have a kinetic half life which is at least twice as long as the kinetic half life of the slowest silicone containing composition. At least one component of the reaction mixture comprises at least one hydroxyl group. The resulting silicone hydrogels are surprisingly easy to process, and display an exceptional balance of properties including stability, haze, water content and oxygen permeability. By introducing an anionic component into to reactive mixture as a slow reacting component, ionic silicone hydrogels with good stability and a desirable uptake profile can be produced.

[0015] The silicone hydrogel polymers of the present invention display stable modulus. As used herein, stable modulus are those which increase less than about 30%, and in some embodiments less than about 20% over 1, 3, 6 or 9 sterilization cycles (121°C and 30 minutes).

[0016] As used herein, "diluent" refers to a non-reactive solvent for the reactive components. Diluents do not react to form part of the biomedical devices.

[0017] As used herein, a "biomedical device" is any article that is designed to be used while either in or on mammalian tissues or fluid, and in or on human tissue or fluids. Examples of these devices include but are not limited to catheters, implants, stents, and ophthalmic devices such as intraocular lenses, punctal plugs and contact lenses. The biomedical devices may be ophthalmic devices, particularly contact lenses, most particularly contact lenses made from silicone hydrogels.

[0018] As used herein, the terms "ophthalmic device" refers to products that reside in or on the eye. As used herein, the terms "lens" and "ophthalmic device" refer to devices that reside in or on the eye. These devices can provide optical correction, wound care, drug delivery, diagnostic functionality, cosmetic enhancement or effect, glare reduction, UV blocking or a combination of these properties. Non-limiting examples of ophthalmic devices include lenses, punctal plugs and the like. The term lens (or contact lens) includes but is not limited to soft contact lenses, hard contact lenses, intraocular lenses, overlay lenses, ocular inserts, and optical inserts.

[0019] As used herein "reaction mixture" refers to reactive and non-reactive components (including the diluent) that are mixed together and reacted to form the silicone hydrogels of the present invention. The reactive components are everything in the reaction mixture except the diluent and any additional processing aids which do not become part of the structure of the polymer.

As used herein "(meth)" refers to an optional methyl substitution. Thus, a term such as "(meth)acrylate" denotes both methacrylic and acrylic radicals.

[0020] All percentages in this specification are weight percentages unless otherwise noted.

[0021] As used herein, the phrase "without a surface treatment" or "not surface treated" means that the exterior surfaces of the devices of the present invention are not separately treated to improve the wettability of the device. Treatments which may be foregone because of the present invention include, plasma treatments, grafting, coating and the like. Coatings which provide properties other than improved wettability, such as, but not limited to antimicrobial coatings and the application of color or other cosmetic enhancement, are not considered surface treatment.

[0022] As used herein "silicone macromers" and silicone "prepolymers" mean mono- and multi-functional silicone containing compounds having molecular weights of greater than about 2000.

[0023] As used herein "hydroxyl-containing component" is any component containing at least one hydroxyl group.

[0024] As used herein "kinetic half life" means the time elapsed at the given reaction conditions for 50 % of the reactive component to be consumed. It should be appreciated that the kinetic half life for a given component will be influenced by the other reaction mixture components, as well as the cure conditions selected, as is described in detail herein. Kinetic half life is calculated as described in the examples.

[0025] The kinetic half life ratios calculated herein must be calculated using the kinetic half lives measured from that particular reaction mixture and cure conditions.

[0026] As used herein "monovalent reactive groups" are groups that can undergo free radical and/or cationic polymerization. Non-limiting examples of free radical reactive groups include (meth)acrylates, styryls, vinyls, vinyl ethers, C_{1-6}alkyl(meth)acrylates, (meth)acrylamides, C_{1-6}alkyl(meth)acrylamides, N-vinyllactams, N-vinylamides, C_{2-12}alkenyls, C_{2-12}alkenylphenyls, C_{2-12}alkenylnaphthyls, C_{2-6}alkenylphenylC_{1-6}alkyls, O-vinylcarbamates and O-vinylcarbonates. Non-limiting examples of cationic reactive groups include vinyl ethers or epoxide groups and mixtures thereof. Non-limiting examples of free radical reactive groups include (meth)acrylate, acryloxy, (meth)acrylamide, and mixtures thereof.

[0027] As used herein "ionic" components include anionic components, cationic components, zwitterionic components and mixtures thereof. Ionic components include salts of ionic compounds and precursors which can be converted to ionic form via protonation, deprotonation or mild hydrolysis, such as azalactones disclosed in US 4810764 and US6902812, which are converted to amino acids via hydrolysis.

[0028] In the present invention the components are selected to react at specific points in the reaction. For example, "fast reacting" components are selected to polymerize primarily at the beginning of the overall copolymerization reaction, while the slow reacting hydrophilic monomer is selected to polymerize primarily at the end of the overall copolymerization reaction. Fast reacting components include the silicone-containing components, the hydroxyalkyl monomers and some crosslinkers. In one embodiment slow reacting components have kinetic half lives which are at least about two times greater than the fastest silicone containing monomer. Kinetic half lives may be measured as described herein. It should be appreciated that the kinetic half lives are relative to specific formulations.

[0029] Examples of slow reacting groups include (meth)acrylamides, vinyls, allyls and combinations thereof and a least one hydrophilic group. Non-limiting examples of the slow reacting group include from N-vinyl amides, O-vinyl carbamates, O-vinyl carbonates, N-vinyl carbamates, O-vinyl ethers, O-2-propenyl, wherein the vinyl or allyl groups may be further substituted with a methyl group. The slow reacting group may be selected from N-vinyl amides, O-vinyl carbonates, and O-vinyl carbamates.

[0030] Examples of fast reacting groups include (meth)acrylates, styryls, (meth)acryamides and mixtures thereof. Generally (meth)acrylates are faster than (meth)acrylamides, and acrylamides are faster than (meth)acrylamides.

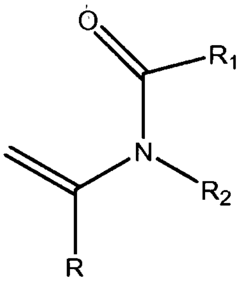
[0031] Throughout the specification, wherever chemical structures are given, it should be appreciated that alternatives disclosed for the substituents on the structure may be combined in any combination. Thus if a structure contained substituents R_1 and R_2, each of which contained three lists of potential groups, 9 combinations are disclosed. The same applies for combinations of properties.

[0032] It has been surprisingly found that by selecting the components of the reaction mixture, silicone hydrogels having a desirable balance of properties many be formed. The reaction mixtures of the present invention comprise about 37 to about 75 wt%, in some embodiments between about 39 and about 70wt% and in other embodiments between about 39 and about 60 wt% of at least one slow-reacting hydrophilic monomer;
at least one reactive silicone-containing component;
and at least one fast reacting crosslinker having at least two fast reacting groups. The slowest reacting silicone-containing component has a kinetic half life which is at least half the kinetic half life of the slow-reacting hydrophilic monomer. At least one of said components comprises at least one hydroxyl group.

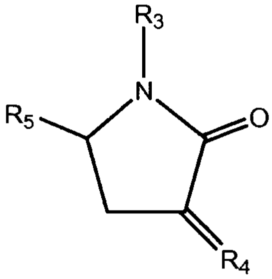
[0033] The first component of the reactive mixture is at least one slow-reacting hydrophilic monomer. The slow-reacting hydrophilic monomer comprises a slow reacting group and a least one hydrophilic group. The reactive group may be selected from N-vinyl amides, O-vinyl carbamates, O-vinyl carbonates, N-vinyl carbamates, O-vinyl ethers, O-2-propenyl, wherein the vinyl or allyl groups may be further substituted with a methyl group. In yet another embodiment the reactive group is selected from N-vinyl amides, O-vinyl carbonates and O-vinyl carbamates. Hydrophilic groups include hydroxyls, amines, ethers, amides, ammonium groups, carboxylic acid, carbamates, combinations thereof and the like. Suitable hydrophilic groups include hydroxyls, ethers, amides, carboxylic acid combinations thereof and the like.

[0034] If a (meth)acrylamide is selected as the slow-reacting hydrophilic monomer, a silicone-containing monomer having a very short kinetic half life, such as an acrylate must be used. Methacrylamides are generally slower reacting that acrylamides, and bulky (meth)acrylamides are slower than smaller (meth)acrylamides. Examples of a suitable (meth)acrylamide include bis-(2-hydroxyethyl) methacrylamide, 2,3-dihydroxypropyl methacrylamide, *N*-[3-(Dimethylamino)propyl]methacrylamide, N-[tris(hydroxymethyl)methyl]acrylamide and methacrylamides substituted with one or two polyethylene glycol chains having 2-10, 2-5 repeating units and the like. Where a methacrylamide is used as the slow-reacting hydrophilic monomer, very fast silicone containing monomer, such as silicone acrylates should be used to provide the desired difference in kinetic half lives. For example, *N*-[3-(Dimethylamino)propyl]methacrylamide may be used as the slow-reacting hydrophilic monomer with silicone acrylates.

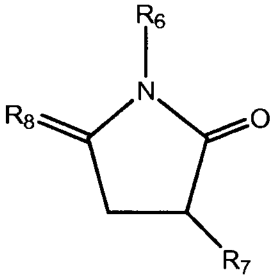
[0035] The slow-reacting hydrophilic monomer may be selected from N-vinylamide monomer of Formula I, a vinyl pyrrolidone of Formula II-IV, n-vinyl piperidone of Formula V :



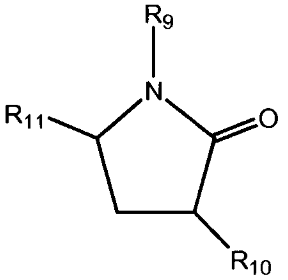
Formula I



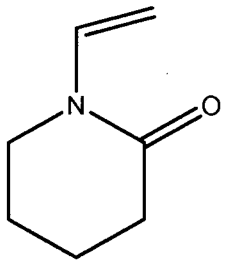
Formula II



Formula III



Formula IV



Formula V

wherein R is H or methyl, or R is H;

R_1, R_2, R_3, R_6, R_7, R_{10}, and R_{11} are independently selected from H, CH_3, CH_2CH_3, $CH_2CH_2CH_3$, $C(CH_3)_2$;

R_4 and R_8 are independently selected from CH_2, $CHCH_3$ and $-C(CH_3)$;

R_5 is selected from H, methyl, ethyl, ; and

R_9 is selected from $CH=CH_2$, $CCH_3=CH_2$, and $CH=CHCH_3$.

[0036] In one embodiment the total number of carbon atoms in R_1 and R_2 is 4 or less, and R_1 and R_2 may be methyl.

[0037] The slow-reacting hydrophilic monomer may be selected from the N-vinyl amide monomer of Formula I or a vinyl pyrrolidone of Formula II or IV. Suitably R_6 is methyl, R_7 is hydrogen, R_9 is $CH=CH_2$, R_{10} and R_{11} are H.

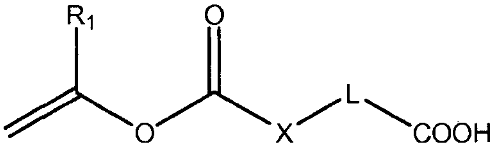
[0038] The slow-reacting hydrophilic monomer may be selected from ethylene glycol vinyl ether (EGVE), di(ethylene glycol) vinyl ether (DEGVE), N-vinyl lactams, including N-vinyl pyrrolidone (NVP), 1-methyl-3-methylene-2-pyrrolidone, 1-methyl-5-methylene-2-pyrrolidone, 5-methyl-3-methylene-2-pyrrolidone; 1-ethyl-5-methylene-2-pyrrolidone, N-methyl-3-methylene-2-pyrrolidone, 5-ethyl-3-methylene-2-pyrrolidone, 1-n-propyl-3-methylene-2-pyrrolidone, 1-n-propyl-5-methylene-2-pyrrolidone, 1-isopropyl-3-methylene-2-pyrrolidone, 1-isopropyl-5-methylene-2-pyrrolidone, N-vinyl-N-methyl acetamide (VMA), N-vinyl-N-ethyl acetamide, N-vinyl-N-ethyl formamide, N-vinyl formamide, N-vinyl acetamide, N-vinyl isopropylamide, allyl alcohol, N-vinyl caprolactam, N-2-hydroxyethyl vinyl carbamate, N-carboxyvinyl-β-alanine (VINAL), N-carboxyvinyl-α-alanine and mixtures thereof.

[0039] Thus, the slow-reacting hydrophilic monomer may selected from NVP, VMA and 1-methyl-5-methylene-2-pyrrolidone. The slow-reacting hydrophilic monomer may comprise NVP.

[0040] The reactive mixture further comprises at least one slow reacting anionic component.

[0041] Suitable reactive groups for the ionic components include N-vinyl amides, O-vinyl carbamates, O-vinyl carbonates, N-vinyl carbamates, O-vinyl ethers, O-2-propenyl, wherein the vinyl or allyl groups may be further substituted with a methyl group and in some embodiments methacrylamide reactive groups. Preferred reactive groups include vinyl ethers, vinyl carbamates, vinyl carbonates, and vinyl amides. The anionic components also comprise at least one anionic group selected from carboxylic acids, sulfonic acids, and their salts and mixtures thereof.

[0042] Examples of anionic components include 4-acrylamidobutanoic acid (ACAII), 3-acrylamidopropionic acid, 5-acrylamidopentanoic acid, 3-acrylamido-3-methylbutanoic acid (AMBA), N-vinyloxycarbonyl-α-alanine, N-vinyloxycarbonyl-β-alanine (VINAL), reactive sulfonate salts, including, vinyl sulphonate sodium salt, vinyl sulphonate salt, acetic acid, 2-carboxymethoxy)-,1-ethe-nylester, of Formula



Where R_1 is H or methyl, X is O or NR_{16}, R_{16} is H or C_{1-3} alkyl), and L is divalent C_{1-4} alkyl group; and mixtures thereof.

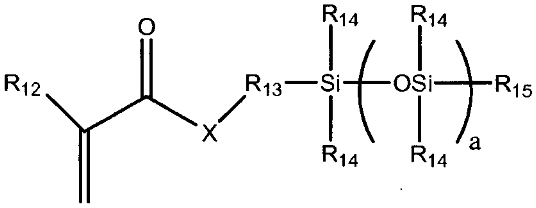
[0043] The slow-reacting anionic component may be selected from the group consisting of N-vinyloxycarbonyl-α-alanine; N-vinyloxycarbonyl-β-alanine (VINAL); vinyl sulphonate sodium salt; acetic acid, 2-(carboxymethoxy)-,1-ethenylesters of the above Formula, mixtures thereof and the like.

[0044] The ionic components are present in the reactive mixture in an amount below about 20 mole%, 15 mole %, between about 0.5 and about 10 mole %, between about 0.5 and about 5 mole %, based upon all components in the reaction mixture.

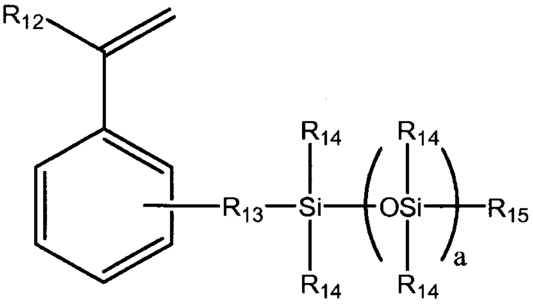
[0045] All of the slow-reacting components may have the same reactive functionality, for example vinyl functionality.

[0046] The slow reacting hydrophilic monomers are present in amounts to provide wettability to the resulting polymer. Wettability may be measured via contact angle, and desirable contact angles are less than about 80°, less than about 70° and in some embodiments less than about 60°.

[0047] The at least one silicone-containing monomer is monofunctional and comprises (a) a fast reacting group and (b) a polydialkyl siloxane chain. The silicon-containing monomer may comprise a fast reacting group selected from (meth)acrylates, styryls, (meth)acrylamides and mixtures thereof. The at least one silicone-containing monomer may also contain at least one fluorine. The silicone-containing component may be selected from mono (meth)acryloxyalkyl polydialkylsiloxane monomer of Formula VII or the styryl polydialkylsiloxane monomer of Formula VIII:



Formula VII



Formula VIII

wherein R_{12} is H or methyl;

X is O or NR_{16};

Each R_{14} is independently a phenyl or C_1 to C_4 alkyl which may be substituted with fluorine, hydroxyl or ether, or each R_{14} is independently selected from ethyl and methyl groups. All R_{14} may be methyl;

R_{15} is an unsubstituted C_1 to C_4 alkyl;

R_{13} is a divalent alkyl group, which may further be functionalized with a group selected from the group consisting of ether groups, hydroxyl groups, carbamate groups and combinations thereof, and C_1-C_6 alkylene groups which may be substituted with ether, hydroxyl and combinations thereof, or C_1 or C_3-C_6 alkylene groups which may be substituted with ether, hydroxyl and combinations thereof;

a is 2 to 50, and in some embodiments 5 to 15.

[0048] R_{16} is selected from H, C_{1-4} alkyls, which may be further substituted with one or more hydroxyl groups, or may be H or methyl.

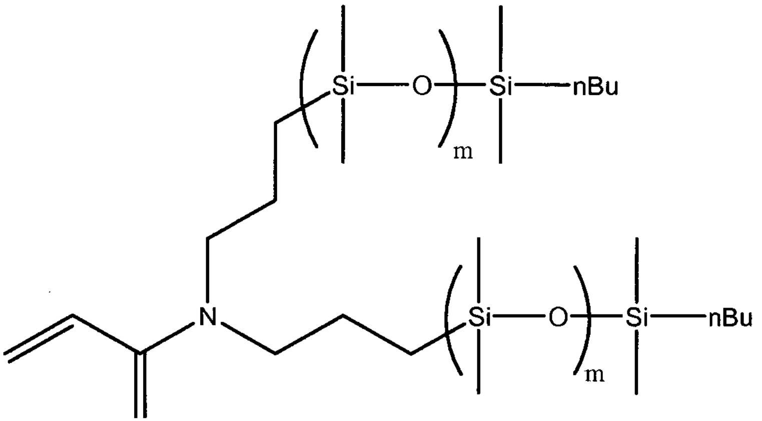
[0049] R_{12} and each R_{14} may be methyl.

[0050] At least one R_{14} may be 3,3,3-trifluoropropyl.

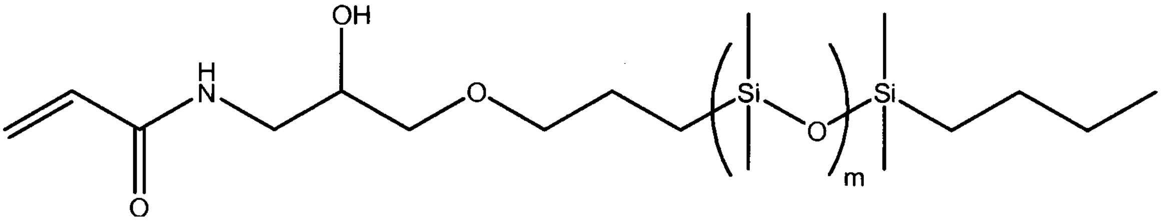
[0051] Examples of suitable silicone-containing monomers include monomethacryloxyalkylpolydimethylsiloxane methacrylates selected from the group consisting of monomethacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane, monomethacryloxypropyl terminated mono-n-methyl terminated polydimethylsiloxane, monomethacryloxypropyl terminated mono-n-butyl terminated polydiethylsiloxane, monomethacryloxypropyl terminated mono-n-methyl terminated polydiethylsiloxane, N-(2,3-dihydroxypropane)-N'-(propyl tetra(dimethylsiloxy) dimethylbutylsilane)acrylamide, α-(2-hydroxy-1-methacryloxypropyloxypropyl)-ω-butyl-decamethylpentasiloxane, and mixtures thereof.

[0052] The silicone-containing component may be selected from the group consisting of monomethacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane, monomethacryloxypropyl terminated mono-n-methyl terminated polydimethylsiloxane, N-(2,3-dihydroxypropane)-N'-(propyl tetra(dimethylsiloxy) dimethylbutylsilane)acrylamide, α-(2-hydroxy-1-methacryloxypropyloxypropyl)-ω-butyl-decamethylpentasiloxane, and mixtures thereof.

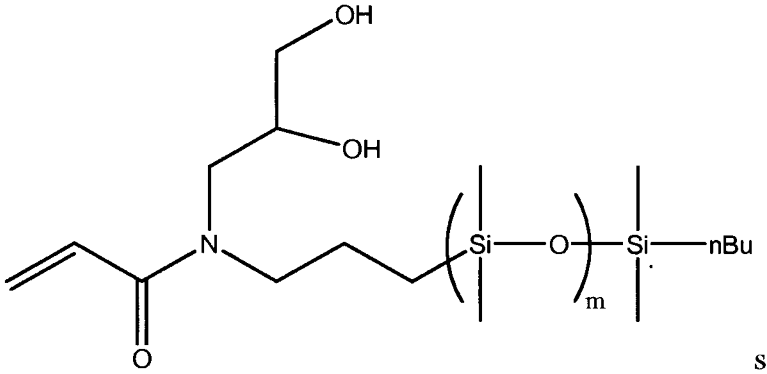
[0053] The silicone containing component may be selected from acrylamide silicones of US20110237766, and particularly the silicone monomers expressed in the following general formulae (s1) through (s6).



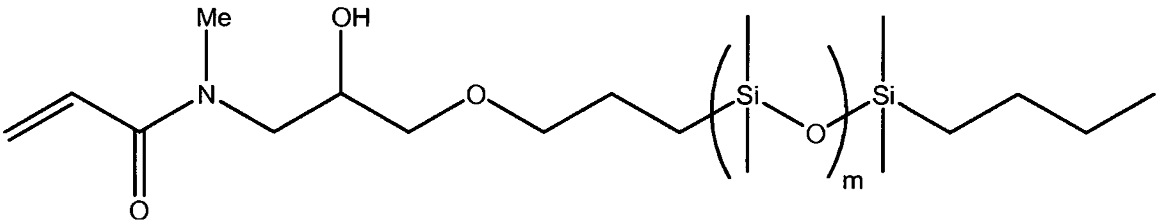
s1



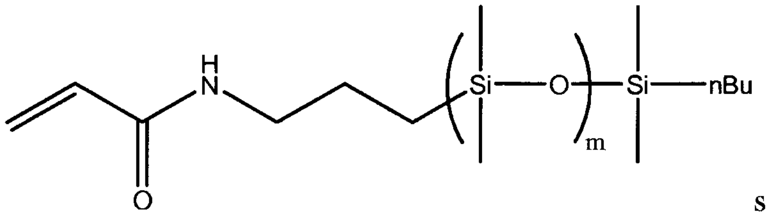
s2



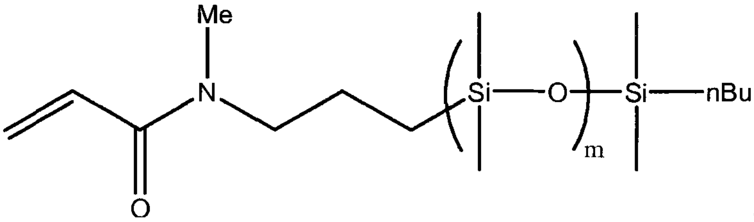
s3



s4



s5



s6

wherein m is 4-12 or 4-10.

[0054] Additional silicone containing components having one or more polymerizable groups may also be included. Any additional disclosed silicone components having the herein disclosed reactive groups may be included. Examples include silicone containing monomers displaying branched siloxane chains such as SiMAA and TRIS. Because the anionic components are slow reacting, the silicone hydrogels of the present invention may comprise fast reacting silicones comprising trimethylsiloxy siloxane (TMS) groups, such as SiMAA and TRIS, even in relatively large amounts up to about 20 wt%. However, neither SiMAA nor TRIS are effective as the main silicone containing component where oxygen permeabilities of greater than about 70 or 80 Dk are desired. Accordingly, in one embodiment the amount of TRIS in the formulation is less than about 15%, 10% and less than 5%, or may contain no TRIS.

[0055] The at least one silicone-containing component is present in the reactive mixture in an amount sufficient to provide the desired oxygen permeability. It is a benefit of the present invention that oxygen permeabilities greater than about 70 barrers, greater than about 80 barrer, greater than about 90 barrer, or greater than about 100 barrer may be achieved. Suitable amounts will depend on the length of the siloxane chain included in the silicone-containing monomers, with silicone-containing monomers having longer chains requiring less monomer. Amounts include from about 20 to about 60 weight%, or from about 30 to about 55 weight %.

[0056] In one embodiment the total amount of silicon in the reactive mixture (excluding diluent) is between about 9 and 14 wt% and between about 9 and 13%. Limiting the amount of silicon, in combination balancing the amount of the slow-reacting hydrophilic monomer and the other reactive components, provides the desirable combination of properties achieved by the present invention. It is a benefit of the present application that silicone hydrogels having the combination oxygen permeabilities and water contents may be formed with only moderate amounts (less than 14 wt%) silicon.

[0057] The slow-reacting hydrophilic monomer and the at least one silicone-containing monomer are selected such that the ratio of the kinetic half life of the slow-reacting hydrophilic monomer to the kinetic half life of the slowest silicone-containing component is at least about 2, at least about 3 or at least about 5.

[0058] As part of the present invention it is desirable to polymerize long chains of the slow-reacting hydrophilic monomer. A substantial amount of slow-reacting hydrophilic monomer must polymerize late in the process in order to achieve the desired balance of properties. In one embodiment this is characterized by the ratio (unit-less) of the concentrations (expressed in μmol/g) of the slow-reacting hydrophilic monomer to the slowest reacting silicone-containing monomer at 90% conversion of the slowest reacting silicone-containing monomer ("conversion ratio"). The conversion ratio may be greater than about 10, at least about 20orat least about 30.

[0059] The reaction mixture may be substantially free of TRIS, and/or substantially free of silicone containing macromers or prepolymers.

[0060] At least one of the components of the reaction mixture must contain at least one hydroxyl group. The hydroxyl may be contained on the silicone-containing monomer, an additional monomer or a combination thereof. It is preferred that the kinetic half life of the hydroxyl-containing component be close to the kinetic half life of the silicone containing monomers. Preferred kinetic half life ratios of the hydroxyl- containing component to the silicone containing monomer include about 0.75 to about 1.5 and about 0.8 to 1.2. The hydroxyl containing components may have the same reactive functionality as the silicone-containing monomers.

[0061] Also, (meth)acrylate monomers with hydroxyl group(s), such as but not limited to SiMAA, and HEMA, have been found to be better at compatibilizing NVP, VMA and other amide containing monomers, than (meth)acrylamide monomers with hydroxyl group(s). Thus in one embodiment where clear lenses with dynamic advancing contact angles of less than about 80° are desired, the hydroxyl-containing monomers comprising (meth)acrylate monomers.

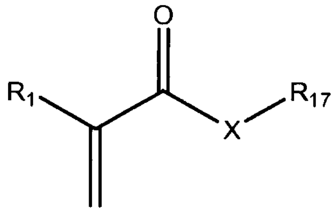
[0062] The hydroxyl-containing components may be present in mole percents which form a molar ratio of hydroxyl groups to the slow-reacting hydrophilic monomer of at least about 0.15, or between about 0.15 and about 0.4. This is calculated by dividing the number of moles of hydroxyl groups in the hydroxyl group-containing monomers (including any hydroxyl groups on the slow-reacting hydrophilic monomer and the silicone-containing monomer) by the number of moles of the slow-reacting hydrophilic monomer per a given mass of the monomer mix. In this embodiment, for a reaction mixture comprising HO-mPDMS, HEMA, EGVE and NVP, the hydroxyl groups on each of HO-mPDMS, HEMA and EGVE would be counted. Any hydroxyl groups present in the diluent (if used) are not included in the calculation. The at least one silicone-containing monomer may comprise at least one hydroxyl group.

[0063] Alternatively, the molar ratio of all hydroxyl groups on reaction components in the reaction mixture to silicon (HO:Si) is between about 0.16 and about 0.4. The molar ratio is calculated by dividing molar concentration of hydroxyl groups in the components of the reactive mixture (other than any hydroxyls which are part of the slow-reacting hydrophilic monomer or diluents) by the molar concentration of silicon. In this embodiment both the hydroxyalkyl monomers and any hydroxyl-containing silicone components are included in the calculation. Thus, in calculating the HO:Si ratio of the reaction mixture comprising HO-mPDMS, HEMA, NVP and EGVE, only the hydroxyl groups on each of HO-mPDMS, HEMA would be counted in calculating the HO:Si.

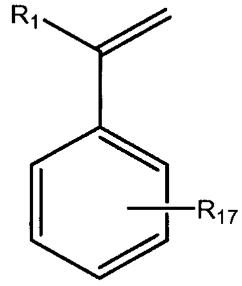
[0064] In another embodiment the molar ratio of hydroxyl groups in non-silicone containing components (other than any hydroxyls which are part of the slow-reacting hydrophilic monomer or diluents) to silicon is between about 0.13 and about 0.35.. Thus, in calculating the HO_{non-Si}:Si ratio of the reaction mixture comprising HO-mPDMS, HEMA, EGVE, and NVP only the hydroxyl groups on, HEMA would be counted in calculating the HO_{non-Si}:Si ratio.

[0065] It will be appreciated that the minimum amount of hydroxyl component will vary depending upon a number of factors, including, the number of hydroxyl groups on the hydroxyalkyl monomer, the amount, molecular weight and presence or absence of hydrophilic functionality on the silicone containing components. For example, where HEMA is used as the hydroxyalkyl monomer and mPDMS is used in amounts about 38wt% as the sole silicone containing monomer, at least about 8wt% HEMA (0.16 HO:Si) is included to provide the desired haze values. However, when lesser amounts of mPDMS are used (about 20%), as little as about 2 or 3% HEMA provides silicone hydrogel contact lenses having haze values below about 50%. Similarly, when the formulation includes substantial amounts of a hydroxyl-containing silicone component (such as greater than about 20 wt% HO-mPDMS), amounts of HEMA as low as about 7 wt% (0.13 HO:Si, or 0.24 HO_{total}:Si) may provide the desired level of haze.

[0066] Suitable hydroxyl-containing monomers include hydroxyalkyl (meth)acrylate or (meth)acrylamide monomer of Formula IX or a styryl compound of Formula X:



FORMULA IX



FORMULA X

wherein R_1 is H or methyl,

X is O or NR_{16}, R_{16} is a H, C_1 to C_4 alkyl, which may be further substituted with at least one OH, methyl or 2-hydroxyethyl and

R_{17} is selected from C_2-C_4 mono or dihydroxy substituted alkyl, and poly(ethylene glycol) having 1-10 repeating units; or 2-hydroxyethyl, 2,3-dihydroxypropyl, 2-hydroxypropyl.

[0067] R_1 may be H or methyl, X may be oxygen and R is selected from C_2-C_4 mono or dihydroxy substituted alkyl, and poly(ethylene glycol) having 1-10 repeating units. R_1 may be methyl, X is oxygen and R is selected from C_2-C_4 mono or dihydroxy substituted alkyl, and poly(ethylene glycol) having 2-20 repeating units, and alternatively R_1 methyl, X is oxygen and R is selected from C_2-C_4 mono or dihydroxy substituted alkyl. Suitably, at least one hydroxyl group may be on the terminal end of the R alkyl group.

[0068] Examples of suitable hydroxyalkyl-containing monomers include 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 1-hydroxypropyl-2-(meth)acrylate, 2-hydroxy-2-methyl-propyl (meth)acrylate, 3-hydroxy-2,2-dimethyl-propyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, glycerol (meth)acrylate, 2-hydroxyethyl (meth)acrylamide, polyethyleneglycol monomethacrylate, bis-(2-hydroxyethyl) (meth)acrylamide, 2,3-dihydroxypropyl (meth)acrylamide, and mixtures thereof.

[0069] The hydroxyl-containing monomer may be selected from the group consisting of 2-hydroxyethyl methacrylate, glycerol methacrylate, 2-hydroxypropyl methacrylate, hydroxybutyl methacrylate, 3-hydroxy-2,2-dimethyl-propyl methacrylate, and mixtures thereof.

[0070] The hydroxyl-containing monomer may comprise 2-hydroxyethyl methacrylate, and in another embodiment comprises 3-hydroxy-2,2-dimethyl-propyl methacrylate. The hydroxyl-containing monomer may comprise glycerol methacrylate.

[0071] The reactive mixture may further comprise additional hydrophilic monomers. Any hydrophilic momomers used to prepare hydrogels may be used. For example monomers containing acrylic groups (CH_2=CROX, where R is hydrogen or C_{1-6}alkyl an X is O or N) or vinyl groups (-C=CH_2) may be used. Examples of additional hydrophilic monomers are N,N-dimethylacrylamide, polyethyleneglycol monomethacrylate, methacrylic acid, acrylic acid, combinations thereof and the like.

[0072] If the additional hydrophilic monomers have kinetic half lives which are intermediate to the slow reacting hydrophilic monomers and silicone containing components as defined herein, their concentrations in the formulations of the present invention may be limited to concentrations which do not provide the lens with an advancing contact angle higher than about 80°. As used herein, "intermediate" half life is one that is between 20% and 70% faster than the slowest reacting silicone component. For example, if the additional hydrophilic monomer is N,N-dimethylacrylamide, the amount of the additional hydrophilic monomer is limited to below about 3 wt% in cases where uncoated lenses are desired. Where the lens is to be surface modified, higher amounts of additional monomers may be included.

[0073] The reaction mixtures of the present invention further comprise at least one crosslinker which has a kinetic half life less than or equal to the kinetic half life of at least one of the silicone-containing monomers included in the reaction mixture. A crosslinker is a monomer with two or more polymerizable double bonds. It has been found that when the kinetic half life of the crosslinker is longer than at least one of the silicone-containing monomers, the resulting hydrogel displays decreased modulus and increased water content. Surprisingly, the reaction rate of the crosslinker can be substantially reduced by the inclusion of a UV absorbing compound. This increases the kinetic half life, and in some systems changed the reaction order, such that the crosslinker reacted more slowly that the silicone-containing monomers. In this circumstance it may be desirable to use a crosslinker with a faster reaction rate in the presence of the selected UV absorber.

[0074] Suitable crosslinkers include ethylene glycol dimethacrylate ("EGDMA"), trimethylolpropane trimethacrylate ("TMPTMA"), glycerol trimethacrylate, polyethylene glycol dimethacrylate (wherein the polyethylene glycol preferably has a molecular weight up to, e.g., about 5000), and other polyacrylate and polymethacrylate esters, such as the end-capped polyoxyethylene polyols described above containing two or more terminal methacrylate moieties. The crosslinker may be used in the usual amounts, e.g., from about 0.000415 to about 0.0156 mole per 100 grams of reactive components in the reaction mixture. Alternatively, if the hydrophilic monomers and/or the silicone containing monomers act as the crosslinking agent, the addition of an additional crosslinking agent to the reaction mixture is optional. Examples of hydrophilic monomers which can act as the crosslinking agent and when present do not require the addition of an additional crosslinking agent to the reaction mixture include polyoxyethylene polyols described above containing two or more terminal methacrylate moieties.

[0075] An example of a silicone containing monomer which can act as a crosslinking agent and, when present, does not require the addition of a crosslinking monomer to the reaction mixture includes α, ω-bismethacryloypropyl polydimethylsiloxane.

[0076] The reaction mixtures can also contain multiple crosslinkers depending on the reaction rate of the hydrophilic component. With very slow reacting hydrophilic components (e.g. VMA, EGVE, DEGVE) crosslinkers having slow reacting functional groups (e.g. di-vinyl, tri-vinyl, di-allyl, tri-allyl) or a combination of slow reacting functional groups and fast reacting functional groups (e.g. HEMAVc, allylmethacrylate) can be combined with crosslinkers having fast reacting functional groups to improve the retention of the polymers of the slow-reacting monomers in the final hydrogel.

[0077] The reaction mixture may comprise at least two crosslinkers, at least one fast reacting crosslinker having at least two fast reacting groups which will react with the silicone components and hydroxyl-containing components and at least one slow reacting crosslinker having at least two slow reacting groups which react with the slow reacting hydrophilic monomer. This mixture of fast and slow reacting crosslinkers provides the final polymer with improved resilience and recovery, particularly on the surface of the lens. Examples of suitable first crosslinkers include those having only (meth)acrylate functionality, such as EGDMA, TEGDMA and combinations thereof. Examples of suitable second crosslinkers include those having only vinyl functionality, such as triallyl cyanurate (TAC). When mixtures are used, suitable amounts of all crosslinker in the reactive mixture include between about 0.10% and about 2%, or between about 0.10% and about 1%, excluding diluent respectively. In another embodiment the total amount of all crosslinker in the reactive mixtures is between 0.7 to about 6.0 mmol/100 g of polymerizable components; between about 0.7 to about 4.0 mmoles per 100 g of reactive components. The fast and slow reacting crosslinkers are present in respective amounts of about 0.3 to about 2.0 mmol/100 g of polymerizable components; or between about 0.4 to about 2.0 mmoles per 100 g of reactive components.

[0078] The reaction mixture may also comprise at least one UV absorbing compound. Surprisingly, UV absorbing compounds can have a substantially different impact on the reaction kinetics of the reactive components in the reaction mixtures of the present invention. For example, it has been found that benzotriazoles substantially slow the rate of reaction for NVP and TEGDMA is some systems much more than the reaction rates of the silicone-containing components. In the case of NVP, this is beneficial, as it provides additional processing flexibility and an exceptional balance of properties, including water contents in excess of about 60%, haze values less than about 50%, less than about 10%, advancing contact angles less than about 60° and Dk's greater than about 80. When the silicone hydrogel will be used as an ophthalmic device it may be desirable to incorporate a reactive UV absorbing compound in the reaction mixture so that the resulting silicone hydrogel will be UV absorbing. However, non-reactive UV absorbing compounds may be used solely to achieve the desired reaction kinetics. Alternatively solution filters may be used. It is believed that the UV absorbers in the reactive mixtures block incident light below about 370 nm which alters the spectrum of light being imposed on the visible photoinitiator. This tends to reduce the rate of initiation as well as lower the concentration of initiator radicals present, which in turn is believed to have a significant impact on the rate of polymerization of the monomers. Typically, the monomers which are likely to be most significantly impacted are the slowest and fastest. In several of the examples included herein, NVP (slowest) and TEGDMA (the fastest) are the most sensitive to the presence of the UV absorber.

[0079] Suitable UV absorbers may be derived from 2-(2'-hydroxyphenyl)benzotriazoles, 2-hydroxybenzophenones, 2-hydroxyphenyltriazines, oxanilides, cyanoacrylates, salicylates and 4-hydroxybenzoates; which may be further reacted to incorporate reactive polymerizable groups, such as (meth)acrylates. Specific examples of UV absorbers which include polymerizable groups include 2-(2'-hydroxy-5-methacrylyloxyethylphenyl)-2H-benzotriazole (Norbloc), 5-vinyl and 5-isopropenyl derivatives of 2-(2,4-dihydroxyphenyl)-2H-benzotriazole and 4-acrylates or 4-methacrylates of 2-(2,4-dihydroxyphenyl)-2H-benzotriazole or 2-(2,4-dihydroxyphenyl)-1,3-2H-dibenzotriazole , mixtures thereof and the like. When a UV absorber is included, it may be included in amounts between about 0.5 and about 4 wt%, and suitably between about 1 wt% and about 2 wt%.

[0080] A polymerization initiator is preferably included in the reaction mixture. Either thermal, photoinitiation or a combination thereof may be used. In one embodiment, the reaction mixtures of the present invention comprise at least one photoinitiator. The use of photoinitiation provides desirable cure times (time to reach essentially complete cure) of less than about 30 minutes, less than about 20 minutes or less than about 15 minutes. The photopolymerization systems also greater flexibility in tailoring the properties of the resulting silicone hydrogel through the use of UV absorbers in the reaction mixtures. Suitable photoinitiator systems include aromatic alpha-hydroxy ketones, alkoxyoxybenzoins, acetophenones, acylphosphine oxides, bisacylphosphine oxides, and a tertiary amine plus a diketone, mixtures thereof and the like. Illustrative examples of photoinitiators are 1-hydroxycyclohexyl phenyl ketone, 2-hydroxy-2-methyl-1-phenyl-propan-1-one, bis(2,6-dimethoxybenzoyl)-2,4-4-trimethylpentyl phosphine oxide (DMBAPO), bis(2,4,6-trimethylbenzoyl)-phenyl phosphineoxide (Irgacure 819), 2,4,6-trimethylbenzyldiphenyl phosphine oxide and 2,4,6-trimethylbenzoyl diphenylphosphine oxide, benzoin methyl ester and a combination of camphorquinone and ethyl 4-(N,N-dimethylamino)benzoate. Commercially available visible light initiator systems include Irgacure 819, Irgacure 1700, Irgacure 1800, Irgacure 819, Irgacure 1850 (all from Ciba Specialty Chemicals) and Lucirin TPO initiator (available from BASF). Commercially available UV photoinitiators include Darocur 1173 and Darocur 2959 (Ciba Specialty Chemicals). These and other photoinitiators which may be used are disclosed in Volume III, Photoinitiators for Free Radical Cationic & Anionic Photopolymerization, 2nd Edition by J.V. Crivello & K. Dietliker; edited by G. Bradley; John Wiley and Sons; New York; 1998, which is incorporated herein by reference. Suitable thermal initiators include lauryl peroxide, benzoyl peroxide, isopropyl percarbonate, azobisisobutyronitrile, and the like. The initiator is used in the reaction mixture in effective amounts to initiate polymerization of the reaction mixture, e.g., from about 0.1 to about 2 parts by weight per 100 parts of reactive monomer.

[0081] The initiator is used in the reaction mixture in effective amounts to initiate polymerization of the reaction mixture, e.g., from about 0.1 to about 2 parts by weight per 100 parts of reactive monomer. As is shown in the Examples, the concentration of photoinitiator used can affect the reaction kinetics of the reactive components. While increasing the amount of initiator generally decreases the kinetic half live of all the components, the half lives are not affected equally. Thus, the ratio of the slow-reacting hydrophilic monomer and silicone containing monomer can be adjusted by varying the initiator concentration. The effect can be increased by adding or increasing the concentration of inhibitors included in the reactive mixture. Some inhibitors may be included with the monomers which are selected. Inhibitors may also be intentionally added to the reaction mixtures of the present application. The amount of inhibitor which may be included is from about 100 to about 2,500 μgm/gm of reaction mixture.

[0082] Inhibitors may optionally be included. Surprisingly the inclusion of even substantial amounts of BHT, a free radical inhibitor did not substantially change the half life ratios measured. However, inclusion of increasing amounts of inhibitor did change the properties of the resulting lenses, decreasing modulus. Thus, it may be desirable to include at least one inhibitor in the reactive mixture. Free radical inhibitors are compounds that react rapidly with propagating radicals to produce stable radical species that terminate the chain. Classes of inhibitors include quinones, substituted phenols, secondary aromatic amines, lactones and nitro compounds. Specific examples of inhibitors include BHT, MEHQ, hydroxyamines, benzofuranone derivatives, molecular oxygen, vitamin E, nitric oxide/nitrogen dioxide mixtures (which form nitroxides in situ) mixtures and combinations thereof and the like.

[0083] Examples of classes of chain transfer agents include alkyl thiols, dithiocarboxylic acid esters, combinations thereof and the like. Examples of controlled free radical initiators include nitroxide mediated polymerization (NMP) (including those disclosed in The Chemistry of Radical Polymerization, 2nd ed. Moad and Solomon, pgs 472-479), atom-transfer radical polymerization (ATRP), including low molecular weight activated organic halides (including those disclosed in The Chemistry of Radical Polymerization, 2nd ed. Moad and Solomon, pgs 488-89 and 492-497), and reversible addition fragmentation (chain) transfer (RAFT) polymerization, including thiocarbonylthio agents (such as those disclosed at including those disclosed in The Chemistry of Radical Polymerization, 2nd ed. Moad and Solomon, pgs 508-514). In the case where controlled free radical initiators are used, they are used as part or all of the initiator system.

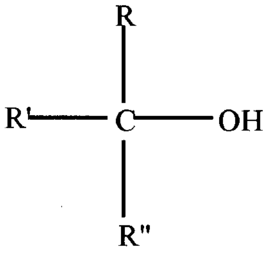
[0084] Polymerization of the reaction mixture can be initiated using the appropriate choice visible or ultraviolet light. Alternatively, initiation can be conducted without a photoinitiator using, for example, e-beam. The initiators may be selected from bisacylphosphine oxides, such as bis(2,4,6-trimethylbenzoyl)-phenyl phosphine oxide (Irgacure 819®) or a combination of 1-hydroxycyclohexyl phenyl ketone and bis(2,6-dimethoxybenzoyl)-2,4-4-trimethylpentyl phosphine oxide (DMBAPO). A preferred method of polymerization initiation is visible light. Bis(2,4,6-trimethylbenzoyl)-phenyl phosphine oxide (Irgacure 819®) is a suitable photoinitiator.

[0085] The reaction mixture may also comprise at least one diluent or may be "neat". If a diluent is used, the selected diluents should solubilize the components in the reactive mixture. It will be appreciated that the properties of the selected hydrophilic and hydrophobic components may affect the properties of the diluents which will provide the desired compatibilization. For example, if the reaction mixture contains only moderately polar components, diluents having moderate δp may be used. If however, the reaction mixture contains strongly polar components, the diluent may need to have a high δp. However, as the diluent becomes more hydrophobic, processing steps necessary to replace the diluent with water will require the use of solvents other than water. This may undesirably increase the complexity and cost of the manufacturing process. Thus, it is important to select a diluent which provides the desired compatibility to the components with the necessary level of processing convenience.

[0086] The type and amount of diluent used also effects the properties of the resultant polymer and article. The haze, wettability and wettability of the final article may be improved by selecting relatively hydrophobic diluents and/or decreasing the concentration of diluent used.

[0087] Diluents useful in preparing the devices of this invention include ethers, esters, amides, alcohols, carboxylic acids and combinations thereof. Amides, carboxylic acids and alcohols are preferred diluents, and carboxylic acids, secondary and tertiary alcohols are more preferred diluents.

[0088] Examples of alcohols useful as diluents for this invention include those having the formula



$$R'-\overset{\displaystyle R}{\underset{\displaystyle R''}{C}}-OH$$

wherein R, R' and R" are independently selected from H, a linear, branched or cyclic monovalent alkyl having 1 to 10 carbons which may optionally be substituted with one or more groups including halogens, ethers, esters, aryls, amines, amides, alkenes, alkynes, carboxylic acids, alcohols, aldehydes, ketones or the like, or any two or all three of R, R' and R" can together bond to form one or more cyclic structures, such as alkyl having 1 to10 carbons which may also be substituted as just described, with the proviso that no more than one of R, R' or R" is H.

[0089] It is preferred that R, R' and R" are independently selected from H or unsubstituted linear, branched or cyclic alkyl groups having 1 to 7 carbons. It is more preferred that R, R', and R" are independently selected form unsubstituted linear, branched or cyclic alkyl groups having 1 to 7 carbons. The preferred diluent may have 4 or more, more preferably 5 or more total carbons, because the higher molecular weight diluents have lower volatility, and lower flammability. When one of the R, R' and R" is H, the structure forms a secondary alcohol. When none of the R, R' and R" are H, the structure forms a tertiary alcohol. Tertiary alcohols are more preferred than secondary alcohols. The diluents are preferably inert and easily displaceable by water when the total number of carbons is five or less.

[0090] Examples of useful secondary alcohols include 2-butanol, 2-propanol, menthol, cyclohexanol, cyclopentanol and exonorborneol, 2-pentanol, 3-pentanol, 2-hexanol, 3-hexanol, 3-methyl-2-butanol, 2-heptanol, 2-octanol, 2-nonanol, 2-decanol, 3-octanol, norborneol, and the like.

[0091] Examples of useful tertiary alcohols include tert-butanol, tert-amyl, alcohol, 2-methyl-2-pentanol, 2,3-dimethyl-2-butanol, 3-methyl-3-pentanol, 1-methylcyclohexanol, 2-methyl-2-hexanol, 3,7-dimethyl-3-octanol, 1-chloro-2-methyl-2-propanol, 2-methyl-2-heptanol, 2-methyl-2-octanol, 2-2-methyl-2-nonanol, 2-methyl-2-decanol, 3-methyl-3-hexanol, 3-methyl-3-heptanol, 4-methyl-4-heptanol, 3-methyl-3-octanol, 4-methyl-4-octanol, 3-methyl-3-nonanol, 4-methyl-4-nonanol, 3-methyl-3-octanol, 3-ethyl-3-hexanol, 3-mehtyl-3-heptanol, 4-ethyl-4-heptanol, 4-propyl-4-heptanol, 4-isopropyl-4-heptanol, 2,4-dimethyl-2-pentanol, 1-methylcyclopentanol, 1-ethylcyclopentanol, 1-ethylcyclopentanol, 3-hydroxy-3-methyl-1-butene, 4-hydroxy-4-methyl-1-cyclopentanol, 2-phenyl-2-propanol, 2-methoxy-2-methyl-2-propanol 2,3,4-trimethyl-3-pentanol, 3,7-dimethyl-3-octanol, 2-phenyl-2-butanol, 2-methyl-1-phenyl-2-propanol and 3-ethyl-3-pentanol, and the like.

[0092] Examples of useful carboxylic acids include C_2-C_{16}, carboxylic acids, with one or two carboxylic acid groups and optionally a phenyl group. Specific examples include acetic acid, decanoic acid, dodecanoic acid, octanoic acid, benzylic acid, , combinations thereof and the like.

[0093] A single alcohol or mixtures of two or more of the above-listed alcohols or two or more alcohols according to the structure above can be used as the diluent to make the polymer of this invention.

[0094] The diluent may be selected from secondary and tertiary alcohols having at least 4 carbons. Suitable examples include tert-butanol, tert-amyl alcohol, 2-butanol, 2-methyl-2-pentanol, 2,3-dimethyl-2-butanol, 3-methyl-3-pentanol, 3-ethyl-3-pentanol, 3,7-dimethyl-3-octanol.

[0095] The diluent may be selected from hexanol, heptanol, octanol, nonanol, decanol, tert-butyl alcohol, 3-methyl-3-pentanol, isopropanol, t amyl alcohol, ethyl lactate, methyl lactate, i-propyl lactate, 3,7-dimethyl-3-octanol, dimethyl formamide, dimethyl acetamide, dimethyl propionamide, N methyl pyrrolidinone and mixtures thereof. Additional diluents useful for this invention are disclosed in US patent 6,020,445, and US 2010-0280146 A1 which is incorporated herein by reference.

[0096] The diluent may be water soluble at processing conditions and readily washed out of the lens with water in a short period of time. Suitable water soluble diluents include 1-ethoxy-2-propanol, 1-methyl-2-propanol, t-amyl alcohol, tripropylene glycol methyl ether, isopropanol, 1-methyl-2-pyrrolidone, N,N-dimethylpropionamide, ethyl lactate, dipropylene glycol methyl ether, mixtures thereof and the like. The use of a water soluble diluent allows the post molding process to be conducted using water only or aqueous solutions which comprise water as a substantial component.

[0097] The diluents may be used in amounts up to about 40% by weight of the total of all components in the reactive mixture. The diluent(s) may be used in amounts less than about 30%, for example in amounts between about 2 and about 20% by weight of the total of all components in the reactive mixture.

[0098] It has been found that even amounts of diluent as low as 2-20 wt%, can lower the modulus of the resulting polymer by about 20% and improve wettability of the resulting polymers and lenses.

[0099] The diluent may also comprise additional components to lower the modulus of the resulting polymers and improve the lens curing efficiency and reducing residuals. Components capable of increasing the viscosity of the reactive mixture and/or increasing the degree of hydrogen bonding with the slow-reacting hydrophilic monomer, are desirable. Suitable components include polyamides, polylactams, such as PVP and copolymers thereof, polyols and polyol containing components such glycerin, boric acid, boric acid glycerol esters, polyalkylene glycols, combinations thereof and the like.

[0100] Suitable polylactams include PVP and copolymers comprising repeating units from NVP and hydrophilic monomers. The polylactam is selected from, PVP, and the polyamide comprises DMA.

[0101] When polyamides or polylactams are used they have a molecular weight of between about K12-K120 (about 3900 to about 3,000,000 Dalton M_w) or from K30 to K90 (about 42,000 to about 1,300,000 Dalton M_w).

[0102] Suitable polyalkylene glycols include polyethylene glycol and polypropylene glycols having molecular weight up to about 350 and suitably ess than about 200 gm/mol.

[0103] When used, the polyols, polyol containing components, polyamides and polylactams are used in amounts less than about 5 wt% or from about 0.2 to about 5 wt%. The diluents and co-diluents of the present invention also reduce the residuals remaining in the polymer at the end of the photocure. This provides lenses with more consistent properties, including diameter. The residual slow-reacting hydrophilic component present at the end of cure may be less than about 2 wt% cured polymer ((wt of residual component/wt of cured polymer) * 100%), or less than about 1 wt% and in some cases less than about 0.8 wt%. The reduction in residuals also leads to more consistent lens properties, including lens diameters, which can vary by less than about 0.05 mm.

[0104] The reactive mixture may contain additional components such as, but not limited to, medicinal agents, antimicrobial compounds, reactive tints, pigments, copolymerizable and non-polymerizable dyes, release agents and combinations thereof.

[0105] Combinations of reactive components and diluents include those having from about 20 to about 65 weight % silicone containing monomer, about 37 to about 70 weight % slow-reacting hydrophilic monomer, from about 2 to about 40 weight % of an hydroxyl containing component, from about 0.2 to about 3 weight % of at least one crosslinking monomer, from about 0 to about 3 weight % of a UV absorbing monomer, (all based upon the weight % of all reactive components). The mixture may further comprises between about 20 to about 60 weight % (weight % of all components, both reactive and non-reactive) of one or more diluents.

[0106] The reaction mixtures of the present invention can be formed by any of the methods known to those skilled in the art, such as shaking or stirring, and used to form polymeric articles or devices by known methods.

[0107] For example, the biomedical devices of the invention may be prepared by mixing reactive components and the diluent(s) with a polymerization initiator and curing by appropriate conditions to form a product that can be subsequently formed into the appropriate shape by lathing, cutting and the like. Alternatively, the reaction mixture may be placed in a mold and subsequently cured into the appropriate article.

[0108] Various processes are known for processing the reaction mixture in the production of contact lenses, including spincasting and static casting. Spincasting methods are disclosed in U.S. Pat. Nos. 3,408,429 and 3,660,545, and static casting methods are disclosed in U.S. Pat. Nos. 4,113,224 and 4,197,266. The method for producing contact lenses comprising the polymer of this invention may be by the direct molding of the silicone hydrogels, which is economical, and enables precise control over the final shape of the hydrated lens. For this method, the reaction mixture is placed in a mold having the shape of the final desired silicone hydrogel, i.e., water-swollen polymer, and the reaction mixture is subjected to conditions whereby the monomers polymerize, to thereby produce a polymer/diluent mixture in the shape of the final desired product.

[0109] Referring to Fig. 1, a diagram is illustrated of an ophthalmic lens 100, such as a contact lens, and mold parts 101-102 used to form the ophthalmic lens 100. The mold parts may include a back surface mold part 101 and a front surface mold part 102. As used herein, the term "front surface mold part" refers to the mold part whose concave surface 104 is a lens forming surface used to form the front surface of the ophthalmic lens. Similarly, the term "back surface mold part" refers to the mold part 101 whose convex surface 105 forms a lens forming surface, which will form the back surface of the ophthalmic lens 100. Mold parts 101 and 102 may be of a concavo-convex shape, preferably including planar annular flanges, which surround the circumference of the uppermost edges of the concavo-convex regions of the mold parts 101-102.

[0110] Typically, the mold parts 101-102 are arrayed as a "sandwich". The front surface mold part 102 is on the bottom, with the concave surface 104 of the mold part facing upwards. The back surface mold part 101 can be disposed symmetrically on top of the front surface mold part 102, with the convex surface 105 of the back surface mold part 101 projecting partially into the concave region of the front surface mold part 102. The back surface mold part 101 may be dimensioned such that the convex surface 105 thereof engages the outer edge of the concave surface 104 of the front mold part 102 throughout its circumference, thereby cooperating to form a sealed mold cavity in which the ophthalmic lens 100 is formed.

[0111] The mold parts 101-102 may be fashioned of thermoplastic and are transparent to polymerization-initiating actinic radiation, by which is meant that at least some, and sometimes all, radiation of an intensity and wavelength effective to initiate polymerization of the reaction mixture in the mold cavity can pass through the mold parts 101-102.

[0112] For example, thermoplastics suitable for making the mold parts can include: polystyrene; polyvinylchloride; polyolefin, such as polyethylene and polypropylene; copolymers or mixtures of styrene with acrylonitrile or butadiene, polyacrylonitrile, polyamides, polyesters, cyclic olefin copolymers such as Topas available from Ticona or Zeonor available from Zeon, copolymers and blends of any of the foregoing, or other known material.

[0113] Following polymerization of the reaction mixture to form a lens 100, the lens surface 103 will typically adhere to the mold part surface 104. The steps of the present invention facilitate release of the surface 103 from the mold part surface. The first mold part 101 can be separated from the second mold part 102 in a demolding process. The lens 100 may have adhered to the second mold part 102 (i.e. the front curve mold part) during the cure process and remain with the second mold part 102 after separation until the lens 100 has been released from the front curve mold part 102. Alternatively, the lens 100 can adhere to the first mold part 101.

[0114] The lens 100 may be released from the mold by any process, including contacting with a solvent or dry release. For example, the lens 100 and the mold part to which it is adhered after demolding may be contacted with an aqueous solution. The aqueous solution can be heated to any temperature below the boiling point of the aqueous solution. Heating can be accomplished with a heat exchange unit to minimize the possibility of explosion, or by any other feasible means or apparatus for heating a liquid.

[0115] As used herein, processing includes the steps of removing the lens from the mold and removing or exchanging the diluent with an aqueous solution. The steps may be done separately, or in a single step or stage. The processing temperature may be any temperatures between about 30°C and the boiling point of the aqueous solutions, for example between about 30°C and about 95°C, or between about 50°C and about 95°C.

[0116] The aqueous solution is primarily water. The aqueous solution may be at least about 70 wt% water, at least about 90 weight % water or at least about 95%. The aqueous solution may also be a contact lens packaging solution such as borate buffered saline solution, sodium borate solutions, sodium bicarbonate solutions and the like. The aqueous solution may also include additives, such as surfactants, preservatives, release aids, antibacterial agents, pharmaceutical and nutriceutical components, lubricants, wetting agents, salts, buffers, mixtures thereof and the like. Specific examples of additives which may be included in the aqueous solution include Tween 80, which is polyoxyethylene sorbitan monooleate, Tyloxapol, octylphenoxy (oxyethylene) ethanol, amphoteric 10), EDTA, sorbic acid, DYMED, chlorhexadine gluconate, hydrogen peroxide, thimerosal, polyquad, polyhexamethylene biguanide, mixtures thereof and the like. Where various zones are used, different additives may be included in different zones. Additives may be added to the hydration solution in amounts varying between 0.01% and 10% by weight, but cumulatively less than about 10% by weight.

[0117] Exposure of the ophthalmic lens 100 to the aqueous solution can be accomplished by any method, such as washing, spraying, soaking, submerging, or any combination of the aforementioned. For example, the lens 100 can be washed with an aqueous solution comprising deionized water in a hydration tower.

[0118] Using a hydration tower, front curve mold parts 102 containing lenses 100 can be placed in pallets or trays and stacked vertically. The aqueous solution can be introduced at the top of the stack of lenses 100 so that the solution will flow downwardly over the lenses 100. The solution can also be introduced at various positions along the tower. The trays can be moved upwardly allowing the lenses 100 to be exposed to increasingly fresher solution.

[0119] Alternatively, the ophthalmic lenses 100 may be soaked or submerged in the aqueous solution.

[0120] The contacting step can last up to about 12 hours, up to about 2 hours or from about 2 minutes to about 2 hours; however, the length of the contacting step depends upon the lens materials, including any additives, the materials that are used for the solutions or solvents, and the temperatures of the solutions. Sufficient treatment times typically shrink the contact lens and release the lens from the mold part. Longer contacting times will provide greater leaching.

[0121] The volume of aqueous solution used may be any amount greater than about 1 ml/lens and in some embodiments greater than about 5 ml/lens.

[0122] After separation or demolding, the lenses on the front curves, which may be part of a frame, are mated with individual concave slotted cups to receive the contact lenses when they release from the front curves. The cups can be part of a tray. Examples can include trays with 32 lenses each, and 20 trays that can be accumulated into a magazine.

[0123] Alternatively, the lenses may be submerged in the aqueous solution. Magazines can be accumulated and then lowered into tanks containing the aqueous solution. The aqueous solution may also include other additives as described above.

[0124] The ophthalmic devices, and particularly ophthalmic lenses of the present invention, have a balance of properties which makes them particularly useful. Such properties include clarity, optics, water content, oxygen permeability and advancing contact angle. Thus, the biomedical devices may be contact lenses having a water content of greater than about 55%, greater than about 60% .

[0125] As used herein clarity means substantially free from visible haze. Clear lenses have a haze value of less than about 70%, more preferably less than about 50% or less than about 10%.

[0126] Suitable oxygen permeabilities include those greater than about 80 barrers, greater than about 85 barrer, or at least about 100 barrer.

[0127] Also, the biomedical devices, and particularly ophthalmic devices and contact lenses have moduli which are less than about 150 psi, or less than about 100 psi.

[0128] The biomedical devices, and particularly ophthalmic devices and contact lenses have average contact angles (advancing) which are less than about 80°, less than about 75° or less than about 70°. The articles of the present invention may have combinations of the above described oxygen permeability, water content and contact angle. All combinations of the above ranges are deemed to be within the present invention.

[0129] Human tears are complex and contain a mixture of proteins, lipids and other components which help to keep the eye lubricated. Examples of lipids classes include wax ester, cholesterolesters and cholesterol. Examples of proteins which are found in human tears include lactoferrin, lysozyme, lipocalin, serum albumin, secretory immunoglobulin A.

[0130] Lysozyme is generally present in human tears in substantial concentrations. Lysozyme is bacteriolytic and believed to protect the eye against bacterial infection. The amount of lysozyme which associates with commercially available contact lenses varies greatly from only a few micrograms to over 800 micrograms for etafilcon A contact lenses (commercially available from Johnson & Johnson Vision Care, Inc., under the ACUVUE and ACUVUE2 brand names). Etafilcon A contact lenses have been commercially available for many years and display some of the lowest adverse event rates of any soft contact lens. Thus, contact lenses which uptake substantial levels of lysozyme are desirable. The lenses of the present invention uptake at least about 30 μg, 50 μg, 100 μg, of lysozyme, all from a 2 mg/ml solution over 72 hours incubation at 35°C.

[0131] The form of the proteins in, on and associated with the lens is also important. Denatured proteins are believed to contribute to corneal inflammatory events and wearer discomfort. Environmental factors such as pH, ocular surface temperature, wear time and closed eye wear are believed to contribute to the denaturation of proteins. However, lenses of different compositions can display markedly different protein uptake and denaturation profiles. In one embodiment of the present invention, a majority of the proteins uptaken by the lenses of the present invention are and remain in the native form during wear. In other embodiments at least about 50%, at least about 70 and at least about 80% of uptaken proteins are and remain native after 24 hours, 3 days and during the intended wear period.

[0132] In one embodiment the ophthalmic devices of the present invention also uptake less than about 20%, in some embodiments less than about 10%, and in other embodiments less than about 5% Polyquaternium-1 (dimethyl-bis[(E)-4-[tris(2-hydroxyethyl)azaniumyl] but-2-enyl]azanium trichloride) ("PQ1") from an ophthalmic solution containing 0.001 wt% PQ1).

Hansen Solubility Parameter

[0133] The Hansen solubility parameter, δp may be calculated by using the group contribution method described in Barton, CRC Handbook of Solubility Par., 1st. Ed. 1983, page 85 - 87 and using Tables 13, 14.

Haze Measurement

[0134] Haze is measured by placing a hydrated test lens in borate buffered saline in a clear 20 x 40 x 10 mm glass cell at ambient temperature above a flat black background, illuminating from below with a fiber optic lamp (Dolan-Jenner PL-900 fiber optic light or Titan Tool Supply Co. fiber optic light with 0.5" diameter light guide set at a power setting of 4-5.4) at an angle 66° normal to the lens cell, and capturing an image of the lens from above, normal to the lens cell with a video camera (DVC 1300C:19130 RGB camera with Navitar TV Zoom 7000 zoom lens) placed 14 mm above the lens platform. The background scatter is subtracted from the scatter of the lens by subtracting an image of a blank cell using EPIX XCAP V 2.2 software. The subtracted scattered light image is quantitatively analyzed, by integrating over the central 10 mm of the lens, and then comparing to a -1.00 diopter CSI Thin Lens®, which is arbitrarily set at a haze value of 100, with no lens set as a haze value of 0. Five lenses are analyzed and the results are averaged to generate a haze value as a percentage of the standard CSI lens.

[0135] Alternatively, instead of a -1.00 diopter CSI Thin Lenses®, a series of aqueous dispersions of stock latex spheres (commercially available as 0.49 μm Polystyene Latex Spheres - Certified Nanosphere Size Standards from Ted Pella, Inc., Product Number 610-30) can be used as standards. A series of calibration samples were prepared in deionized water. Each solution of varying concentration was placed in a cuvette (2mm path length) and the solution haze was measured using the above method.

Solution	Concentration	Mean GS
	(wt% x 10^{-4})	
1	10.0	533
2	6.9	439
3	5.0	379
4	4.0	229
5	2.0	172
6	0.7	138
Mean GS = mean gray scale		

A corrective factor was derived by dividing the slope of the plot of Mean GS against the concentration (47.1) by the slope of an experimentally obtained standard curve, and multiplying this ratio times measured scatter values for lenses to obtain GS values.

[0136] "CSI haze value" may be calculated as follows:

$$\text{CSI haze value} = 100\text{x}(\text{GS-BS})/(217\text{-BS})$$

Where GS is gray scale and BS is background scatter.

Water Content

[0137] The water content of contact lenses was measured as follows: Three sets of three lenses are allowed to sit in packing solution for 24 hours. Each lens is blotted with damp wipes and weighed. The lenses are dried at 60°C for four hours at a pressure of 0.4 inches Hg or less. The dried lenses are weighed. The water content is calculated as follows:

$$\%\ \text{water content} = \frac{(\text{wet weight} - \text{dry weight})}{\text{wet weight}} \text{ x } 100$$

[0138] The average and standard deviation of the water content are calculated for the samples and are reported.

Modulus

[0139] Modulus is measured by using the crosshead of a constant rate of movement type tensile testing machine equipped with a load cell that is lowered to the initial gauge height. A suitable testing machine includes an Instron model 1122. A dogbone shaped sample having a 0.522 inch length, 0.276 inch "ear" width and 0.213 inch "neck" width is loaded into the grips and elongated at a constant rate of strain of 2 in/min. until it breaks. The initial gauge length of the sample (Lo) and sample length at break (Lf) are measured. Twelve specimens of each composition are measured and the average is reported. Percent elongation is = [(Lf-Lo)/Lo]x 100. Tensile modulus is measured at the initial linear portion of the stress/strain curve.

Advancing Contact Angle

[0140] All contact angles reported herein are advancing contact angles. The advancing contact angle was measured as follows. Four samples from each set were prepared by cutting out a center strip from the lens approximately 5 mm in width and equilibrated in packing solution. The wetting force between the lens surface and borate buffered saline is measured at 23°C using a Wilhelmy microbalance while the sample is being immersed into or pulled out of the saline. The following equation is used

$$F = 2\gamma p\cos\theta \qquad \text{or} \qquad \theta = \cos^{-1}(F/2\gamma p)$$

where F is the wetting force, γ is the surface tension of the probe liquid, p is the perimeter of the sample at the meniscus and θ is the contact angle. The advancing contact angle is obtained from the portion of the wetting experiment where the sample is being immersed into the packing solution. Each sample was cycled four times and the results were averaged to obtain the advancing contact angles for the lens.

Oxygen Permeability (Dk)

[0141] The Dk is measured as follows. Lenses are positioned on a polarographic oxygen sensor consisting of a 4 mm diameter gold cathode and a silver ring anode then covered on the upper side with a mesh support. The lens is exposed to an atmosphere of humidified 2.1% O_2. The oxygen that diffuses through the lens is measured by the sensor. Lenses are either stacked on top of each other to increase the thickness or a thicker lens is used. The L/Dk of 4 samples with significantly different thickness values are measured and plotted against the thickness. The inverse of the regressed slope is the Dk of the sample. The reference values are those measured on commercially available contact lenses using this method. Balafilcon A lenses available from Bausch & Lomb give a measurement of approx. 79 barrer. Etafilcon lenses give a measurement of 20 to 25 barrer. (1 barrer = 10^{-10} (cm^3 of gas x cm^2)/(cm^3 of polymer x sec x cm Hg)).

Lysozyme, Lipocalin & Mucin Uptake

[0142] Lysozyme uptake was measured as follows: The lysozyme solution used for the lysozyme uptake testing contained lysozyme from chicken egg white (Sigma, L7651) solubilized at a concentration of 2 mg/ml in phosphate saline buffer supplemented by Sodium bicarbonate at 1.37g/l and D-Glucose at 0.1 g/l.

[0143] Three lenses for each example were tested using each protein solution, and three were tested using PBS (phosphate buffered saline) as a control solution. The test lenses were blotted on sterile gauze to remove packing solution and aseptically transferred, using sterile forceps, into sterile, 24 well cell culture plates (one lens per well) each well containing 2 ml of lysozyme solution. Each lens was fully immersed in the solution. 2 ml of the lysozyme solution was placed in a well without a contact lens as a control.

[0144] The plates containing the lenses and the control plates containing only protein solution and the lenses in the PBS, were parafilmed to prevent evaporation and dehydration, placed onto an orbital shaker and incubated at 35°C, with agitation at 100 rpm for 72 hours. After the 72 hour incubation period the lenses were rinsed 3 to 5 times by dipping lenses into three (3) separate vials containing approximately 200 ml volume of PBS. The lenses were blotted on a paper towel to remove excess PBS solution and transferred into sterile conical tubes (1 lens per tube), each tube containing a volume of PBS determined based upon an estimate of lysozyme uptake expected based upon on each lens composition. The lysozyme concentration in each tube to be tested needs to be within the albumin standards range as described by the manufacturer (0.05 micogram to 30 micrograms). Samples known to uptake a level of lysozyme lower than 100 μg per lens were diluted 5 times. Samples known to uptake levels of lysozyme higher than 500 μg per lens (such as etafilcon A lenses) are diluted 20 times.

[0145] 1 ml aliquot of PBS was used for all samples other than etafilcon. 20ml were used for etafilcon A lens. Each control lens was identically processed, except that the well plates contained PBS instead of lysozyme solution.

[0146] Lysozyme uptake was determined using on-lens bicinchoninic acid method using QP-BCA kit (Sigma, QP-BCA) following the procedure described by the manufacturer (the standards prep is described in the kit) and is calculated by subtracting the optical density measured on PBS soaked lenses (background) from the optical density determined on lenses soaked in lysozyme solution.

[0147] Optical density was measured using a SynergyII Micro-plate reader capable for reading optical density at 562nm.

[0148] Lipocalin uptake was measured using the following solution and method. The lipocalin solution contained B Lactoglobulin (Lipocalin) from bovine milk (Sigma, L3908) solubilized at a concentration of 2 mg/ml in phosphate saline buffer (Sigma, D8662) supplemented by sodium bicarbonate at 1.37g/l and D-Glucose at 0.1 g/1.

[0149] Three lenses for each example were tested using the lipocalin solution, and three were tested using PBS as a control solution. The test lenses were blotted on sterile gauze to remove packing solution and aseptically transferred, using sterile forceps, into sterile, 24 well cell culture plates (one lens per well) each well containing 2 ml of lipocalin solution. Each lens was fully immersed in the solution. Control lenses were prepared using PBS as soak solution instead of lipocalin. The plates containing the lenses immersed in lipocalin solution as well as plates containing control lenses immersed in PBS, were parafilmed to prevent evaporation and dehydration, placed onto an orbital shaker and incubated at 35°C, with agitation at 100 rpm for 72 hours. After the 72 hour incubation period the lenses were rinsed 3 to 5 times by dipping lenses into three (3) separate vials containing approximately 200 ml volume of PBS. The lenses were blotted on a paper towel to remove excess PBS solution and transferred into sterile 24 well plates each well containing 1 ml of PBS solution.

[0150] Lipocalin uptake was determined using on-lens bicinchoninic acid method using QP-BCA kit (Sigma, QP-BCA) following the procedure described by the manufacturer (the standards prep is described in the kit) and is calculated by subtracting the optical density measured on PBS soaked lenses (background) from the optical density determined on lenses soaked in lipocalin solution. Optical density was measured using a SynergyII Micro-plate reader capable for reading optical density at 562nm.

[0151] Mucin uptake was measured using the following solution and method. The Mucin solution contained Mucins from bovine submaxillary glands (Sigma, M3895-type 1-S) solubilized at a concentration of 2 mg/ml in phosphate saline buffer (Sigma, D8662) supplemented by sodium bicarbonate at 1.37g/l and D-Glucose at 0.1 g/l.

[0152] Three lenses for each example were tested using Mucin solution, and three were tested using PBS as a control solution. The test lenses were blotted on sterile gauze to remove packing solution and aseptically transferred, using sterile forceps, into sterile, 24 well cell culture plates (one lens per well) each well containing 2 ml of Mucin solution. Each lens was fully immersed in the solution. Control lenses were prepared using PBS as soak solution instead of lipocalin.

[0153] The plates containing the lenses immersed in Mucin as well as plates containing control lenses immersed in PBS were parafilmed to prevent evaporation and dehydration, placed onto an orbital shaker and incubated at 35°C, with agitation at 100 rpm for 72 hours. After the 72 hour incubation period the lenses were rinsed 3 to 5 times by dipping lenses into three (3) separate vials containing approximately 200 ml volume of PBS. The lenses were blotted on a paper towel to remove excess PBS solution and transferred into sterile 24 well plates each well containing 1 ml of PBS solution.

[0154] Mucin uptake was determined using on-lens bicinchoninic acid method using QP-BCA kit (Sigma, QP-BCA) following the procedure described by the manufacturer (the standards prep is described in the kit) and is calculated by subtracting the optical density measured on PBS soaked lenses (background) from the optical density determined on lenses soaked in Mucin solution. Optical density was measured using a SynergyII Micro-plate reader capable for reading optical density at 562nm.

Kinetics

Preparation of Reactive Monomer Mixes: 15 - 20 g batch

[0155] The preparation of the reactive monomer mixtures for the kinetics studies were prepared under yellow light as follows. The components for each kinetics example were weighed into a 20 mL amber borosilicate glass scintillation vial (Wheaton 320 brand; Catalogue # 80076-576, or equivalent). Vials were capped (using PTFE lined green cap, Qorpak; Supplier # 5205/100, Catalogue # 16161-213) and rolled on jar roller until all solids were dissolved and a homogeneous mixtures were obtained.

Degas

[0156] Reactive monomer mixes were degassed under vacuum, under yellow light for 7 - 10 minutes, and back-filling with nitrogen after breaking vacuum. Vials were quickly capped and placed in compartment 1 of a two compartment nitrogen cure box, via the gated aperature, 7, as shown in Figure 2. The conditions in compartment 1 were room temperature and <0.5% oxygen (using continuous nitrogen purge).

Nitrogen Cure Box - Compartment 2

[0157] The oxygen level in both compartments was maintained by continuous/constant nitrogen purge. The temperature in Compartment 2 was maintained by a heater (COY, Laboratory Products Inc.). The nitrogen cure box was allowed to equilibrate for a minimum of 4 hours prior to performing each kinetics study. The degassed reactive mixture (in tightly capped amber vial) was placed in compartment 1 during the equilibration period.

Light Source and Intensity Setting

[0158] As depicted in Figure 3, 2 fluorescent light fixtures (Lithonia Lighting Fluorescent Luminaire (Gas Tube Luminaire), 60 cm x 10.5 cm) each equipped with 2 fluorescent lamps (Philips TLK 40W/03, 58 cm) were arranged in parallel. The cure intensity was attenuated by adjusting the height of the shelf (shown in Figures 2 and 3) relative to the light source. The intensity at a given shelf height was measured by placing the sensor of a calibrated radiometer/photometer on the mirrored surface, consistent with the position of the sample, as shown in Figure 3. The sensor was placed directly under the space between the 2nd and 3rd lamps in the 4 lamps arrangement.

[0159] Using a calibrated analytical balance (4 decimal places) the weight of a clear borosilicate glass scintillation vial (Wheaton 986541) with cap (white cap with polyethylene insert) was determined. The vial with cap was transferred to Compartment 1 of the Nitrogen Cure Box. The cap was unscrewed and using a calibrated 10 - 100 μL Eppendorf Pipet, 100 μL of the Reactive Monomer Mixture was transferred into the vial. The vial was tightly capped, quickly moved into Compartment 2, via door 6, and placed on the mirrored surface 4, as shown in Figure 2. The sample was placed directly under the space between the 2nd and 3rd lamps in the 4 lamps arrangement. The light source 3, was turned on and the sample was exposed for a specified time period. Although the light source was set at 4 - 5 mW/cm^2, the actual intensity reaching the sample is 0.7 - 1.3 mW/cm^2, due the cap on the sample glass vials. After exposure, the light source 3,was turned off and the vial (with cap) was re-weighed to determine the sample weight by difference. Using a calibrated 500 - 5000 μL Eppendorf Pipet, 10 mL HPLC grade methanol was added to the vial.

[0160] Aliquots (100 μL) of the Reactive Monomer Mixture were pipetted into separate borosilicate glass scintillation vials and the above procedure described above was performed to generate samples at the following minimum time points (minutes): 0, 0.25, 0.50, 0.75, 1, 2, 4, 6, 8, 10.

Cured polymers were extracted in methanol overnight by gently shaking at room temperature.

[0161] Extracts were analyzed for residual components by High Performance Liquid Chromatography with UV detection (HPLC/UV) using the following procedures.

[0162] Quantitation of the mPDMS in the extracts was performed against external calibration standards (about 6 - 11, using the response of the n=6 oligomer), typically covering the range of 1 μg/mL - 800 μg/mL. If the concentrations of mPDMS in the extracts were outside the calibration range, the extracts were diluted with methanol to render concentrations within the calibration range for more accurate quantitation.

Chromatographic Conditions

[0163]

Column: Agilent Zorbax Eclipse XDB18, 4.6 x 50 mm x 1.8 μm
Column Temperature: 30 °C
UV Detector: 217 nm
Injection Volume: 20 μL

Mobile Phase

[0164]

Eluent A: De-ionized
Eluent B: Acetonitrile
Eluent C: Isopropanol
Flow Rate: 1 mL/min

Time (mins)	%A	%B	%C
0.0	50	48	2
0.5	50	48	2
2.0	0	60	40
5.0	0	60	40
5.1	0	30	70
8.0	0	30	70
8.1	50	48	2
10.0	50	48	2

[0165] Quantitation of the components in the extracts other than mPDMS was performed against external calibration standards (about 6 - 11) for each component, typically covering the range of 1 μg/mL - 800 μg/mL. If the concentrations of components in the extracts were outside the calibration range, the extracts were appropriately diluted with methanol to render concentrations within the calibration range for more accurate quantitation.

Chromatographic Conditions

[0166]

Column: Agilent Zorbax Eclipse Plus 18, 4.6 x 75 mm x 1.8 μm
Column Temperature: 30 °C
UV Detector: 217 nm
Injection Volume: 5 μL

Mobile Phase

[0167]

Eluent A: De-ionized water with 0.05% H_3PO_4
Eluent B: Acetonitrile with 0.05% H_3PO_4
Eluent C: Methanol
Flow Rate: 1 mL/min

Time (mins)	%A	%B	%C
0	95	5	0
5	95	5	0
15	0	100	0
23	0	100	0
24	0	30	70
28	0	30	70
29	95	5	0
35	95	5	0

Calculations

[0168]

1. At each time point the following values are determined:
The concentration (μg/mL) of each component in the sample extract.
The concentration of each component in the sample extract, expressed as a percent of the sample weight as follows:

$$\%\ \text{Component} = [(\mu\text{g/mL} * \text{Volume of Extract} * \text{Dilution Factor} * 10^{-6}\ \text{g}/\mu\text{g}) / (\text{g Sample Weight})] * 100$$

The percent unreacted component present, expressed as a percent relative to T_0 (where T_0 represented 100 % unreacted component)

$$\%\ \text{at}\ T_x = (\%\ \text{Measured at}\ T_x / \%\ \text{Measured at}\ T_0) * 100$$

2. Using the % Component calculated above, the concentration of each component in μmoles/g, is calculated as follows:

$$\mu\text{moles/g} = (\%\ \text{Component} * 10^3) / (\text{Molecular Weight of Component})$$

3. Using the concentration of each component determined in μmoles/g in step 2, the concentration at Time_x was expressed as

$$\text{Log } [A_x]/[A_o],$$

where $[A_x]$ is the concentration of component A at x minutes and
$[A_o]$ is the concentration of component A at 0 minutes (T_0)

[0169] The expression Log $[A_x]/[A_o]$ was determined for each time point.

[0170] First order kinetics were assumed for determining both the polymerization kinetics rate and half life for each component. The following equations were used for calculating polymerization rate

$$\text{Log}[A]/[A_0]=-kt/2.303$$

and half life

$$\ln[A_0]/[0.5A_0]=kt_{1/2} \text{ or } t_{1/2} = 0.693/k$$

For each component, a plot of Log $[A_x]/[A_0]$ versus time (minutes) was generated. Typically, the data points (x, y) that best correspond to linear growth (shorter cure times) were plotted and the data were fitted to a linear equation.

[0171] Using the slope, the kinetic rate constant (k) of each component was evaluated from the following equation:

$$k \text{ (minute}^{-1}) = \text{Slope} * -2.303$$

[0172] The half-life (minutes) of each component was evaluated from the following equation:

$$t_{1/2} = 0.693/k$$

[0173] The evaluated half-life for each component was compared to the data generated for the percent of each component relative to T_0, at each time point. Typically for each component, the time taken to attain 50% consumption was close to the half-life based on 1st order kinetics In cases where the two were significantly different (typically about 30% for half-life of less than about 1minute, 25% for half-life less than about 2.5 minutes but greater than 1minute and 20% for half-life greater than 2.5 minutes), the data points (x, y) were re-evaluated to generate kinetic rate constants (k) which would provide half-lives (based on 1st order considerations) more consistent (within 20%) with the measured values.

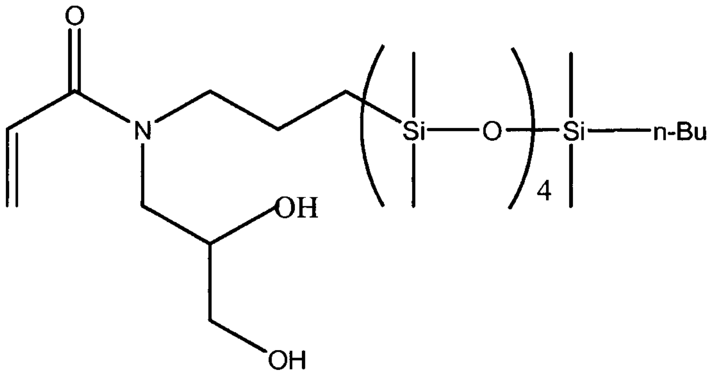
[0174] Some of the other materials that are employed in the Examples are indentified as follows:

EXAMPLES

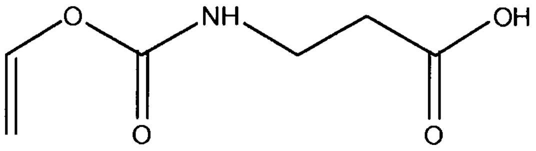
[0175] The following abbreviations are used in the examples below:

FC Front mold curves
BC Back mold curves
SiMAA (3-methacryloxy-2-hydroxypropoxy)propyl-bis(trimethylsiloxy)methylsilane (Also known as SiGMA)
DMA N,N-dimethylacrylamide
HEMA 2-hydroxyethyl methacrylate
HEAA hydroxyethylacrylamide
HBMA 2-hydroxybutyl methacrylate, prepared as in Example XX
HPMA 2-hydroxypropyl methacrylate (ACROS)
DMHEMA dimethylhydroxyethylmethacrylate, prepared as in Example XY
mPDMS 800-1000 MW (M_n) monomethacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane
OH-mPDMS α-(2-hydroxy-1-methacryloxypropyloxypropyl)-ω-butyl-decamethylpentasiloxane, (MW 612g/mol), prepared as in Example 8 of US20100249356 A1
Norbloc 2-(2' -hydroxy-5 -methacrylyloxyethylphenyl)-2H-benzotriazole
D30 3,7-dimethyl-3-octanol
IPA isopropyl alcohol
TAC triallylcyanurate

TEGDMA tetraethyleneglycol dimethacrylate
TRIS 3-methacryloxypropyltris(trimethylsiloxy)silane
CGI 819 bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide EtOAc ethyl acetate
DA decanoic acid
GMMA 2,3-dihydroxypropyl methacrylate
TAA t-amyl alcohol
ETOH ethanol
SA-2 N-(2,3-dihydroxypropane)-N'-(propyl tetra(dimethylsiloxy) dimethylbutylsilane)acrylamide, as shown in Formula XI



VMA N-vinyl-N-methyl acetamide
NVP N-vinylpyrrolidone
BHT butylated hydroxytoluene
PVP poly(N-vinylpyrrolidone)
VINAL an ionic amide containing vinyl ether having the structure



and prepared in Synthetic Preparation 3

[0176] BAE (Boric Acid Ester) was formed as follows:

> 1.24 parts of a 5% (wt) solution of ethylenediaminetetraacetic acid, 299 parts (wt) glycerol and 100 parts (wt) boric acid were added to a reaction flask. The mixture was heated with stirring to 90°C. Vacuum was applied to reduce the pressure to less than 6 torr as the mixture was stirred for 155 minutes, with removal of water vapor. The pressure was reduced to less than 2 torr and the reaction was continued for 2 hours, or longer as needed until the % water of the mixture was reduced to less than 0.2% using a Karl Fischer test.

[0177] BAGE (Boric Acid Glycerol Ester) was formed as follows:

> To BAE prepared as described above was added 624 parts (wt) glycerol with stirring for 60 minutes at 35-40°C.

Example 1 and Comparative Example 1

[0178] A reaction mixture was formed by mixing the components listed in Table 1 and degassed by applying vacuum at ambient temperature for about 17($\pm$3) minutes. The reaction mixture (75 μL) was then dosed at room temperature and <0.5% O_2, into thermoplastic contact lens molds (FC - Zeonor, BC Polypropylene) which had been degassed in N_2 box at RT (Compartment 1, Figure 1) for a minimum of 12 hours prior to dosing. The BC was placed on the FC mold to produce 8 BC/FC assemblies in a pallet. Eight pallets were assembled and moved into the cure compartment (Compartment 2, Figure 1). Pallets were placed on a mirrored surface and a quartz plate (0.50 mm thick) was placed over each pallet. The lenses were cured for 18 minutes, at an intensity of 4 - 5 mW/cm^2, <0.5% O_2, and 50 - 55 °C.

[0179] The molds were manually demolded (lenses remained in FC) and lenses were released in 50/50 IPA/H_2O (8 pallets, 8 lenses per pallet), 1 L solution, 1 hour.

[0180] Lenses were "stepped down" into PS in the following order: 25/75IPA/H_2O (10 mins), H_2O (30 mins), H_2O (10 mins), H_2O (10 mins), and stored in borate buffered packing solution in lens vials and sterilized at 122°C for 30 minutes.

Table 1

Component	Ex. 1 NVP	CE 1 DMA
OH-mPDMS, n=4	40	40
NVP	50.5	0
DMA	0	50.5
HEMA	6.75	6.75
TEGDMA	0.5	0.5
Norblock	2	2
CGI 819	0.25	0.25

Table 2

Ex. #	% H_2O	% Haze	DCA	Mechanicals		Dk
				Mod. (psi)	Elong. (%)	
1	58.4 (0.2)	4 (0)	44 (4)	102.9 (11.4)	220.3 (36.2)	74.7
CE1	59.8 (0.1)	5 (1)	127 (14)	54.1 (7.4)	227.3 (52.3)	48.5

[0181] The lenses of Example 1 exhibited exceptional haze (4%), wettability (DCA 44°), modulus, elongation and Dk. The lenses of Comparative Example 1 exhibited greatly increased contact angle (127°), indicating a marked decrease in wettability. Comparative Example 1 also displayed a substantially reduced modulus (54.1 psi) and oxygen permeability (48.5) compared to Example 1 (102.9 and 74.7, respectively).

Examples 2 and Comparative Example 2

[0182] The polymerization rate and half life for each component in the Formulations of Example 1 and Comparative Example 1 were determined using the procedure described in the kinetics section above. In each Example, for each of the components in the sample extract and at each of the time points the following information is reported, the wt% of each residual component measured (Table 3), % incorporation of each residual component at each time point relative to the % residual measured at T_0 (Table 4), the μmole/g of each residual component at each time point (Table 5) and, log[A]/[A_0] (Table 6), and the polymerization rate constants and half-lives (Tables 7 and 8).

Table 3

	Ex. 2 RESIDUAL MONOMERS WT%					
Cure Time	NVP	HEMA	TEGDMA	Norbloc	CGI 819	OH-mPDMS
0.00	48.687	6.612	0.493	2.036	0.211	36.999
0.25	50.127	5.740	0.377	1.805	0.167	33.584
0.50	50.053	4.958	0.303	1.602	0.129	29.903
1.00	48.037	3.611	0.185	1.152	0.067	22.854
2.00	45.327	1.722	0.072	0.554	0.020	11.709
4.00	37.315	0.520	0.030	0.085	0.002	3.724
6.00	34.959	0.439	0.027	0.037		3.393
8.00	32.155	0.330	0.021	0.016		2.562

(continued)

	Ex. 2 RESIDUAL MONOMERS WT%					
Cure Time	**NVP**	**HEMA**	**TEGDMA**	**Norbloc**	**CGI 819**	**OH-mPDMS**
10.00	24.624					
12.00	21.977					
15.00	17.041					
20.00	8.579					
30.00	3.241					

Table 4

Ex. 2 % Incorporation						
	%	%	%	%	%	%
Cure Time	**NVP**	**HEMA**	**TEGDMA**	**Norbloc**	**CGI 819**	**OH-mPDMS**
0.00	100.00	100.00	100.00	100.00	100.00	100.00
0.25	102.96	86.81	76.49	88.65	79.13	90.77
0.50	102.81	74.99	61.35	78.69	61.15	80.82
1.00	98.67	54.61	37.56	56.59	31.64	61.77
2.00	93.10	26.04	14.55	27.19	9.44	31.65
4.00	76.64	7.86	6.10	4.18	1.04	10.06
6.00	71.80	6.63	5.45	1.81		9.17
8.00	66.04	4.99	4.15	0.77		6.92
10.00	50.58					

Table 5

Ex. 2 RESIDUAL MONOMERS (umoles/g)						
Cure Time (mins)	**NVP**	**HEMA**	**TEGDMA**	**Norbloc**	**CGI 819**	**OH-mPDMS**
0.00	4386.23	508.60	17.25	62.66	5.04	604.57
0.25	4515.93	441.52	13.20	55.55	3.99	548.76
0.50	4509.28	381.39	10.58	49.31	3.08	488.62
1.00	4327.69	277.76	6.48	35.46	1.60	373.43
2.00	4083.51	132.44	2.51	17.04	0.48	191.32
4.00	3361.70	39.99	1.05	2.62	0.05	60.85
6.00	3149.41	33.74	0.94	1.14		55.44
8.00	2896.87	25.37	0.72	0.48		41.86
10.00	2218.40					

Table 6

	NVP	**HEMA**	**TEGDMA**	**Norblock**	**CGI 819**	**OH-mPDMS**
Cure Time	**Log[A]/[A$_0$]**	**Log[A]/[A$_0$]**	Log[A]/[A0]	Log [A]/[A0]	Log[A]/[A0]	Log [A]/[A0]
0.25	0.0127	-0.0614	-0.1164	-0.0523	-0.1017	-0.0421
0.50	0.0120	-0.1250	-0.2122	-0.1041	-0.2136	-0.0925
1.00	-0.0058	-0.2627	-0.4253	-0.2473	-0.4997	-0.2092
2.00	-0.0311	-0.5844	-0.8371	-0.5656	-1.0250	-0.4997
4.00	-0.1155	-1.1044	-1.2146	-1.3784	-1.9814	-0.9972
6.00	-0.1439	-1.1783	-1.2634	-1.7418		-1.0377
8.00	-0.1802	-1.3021	-1.3814	-2.1130		-1.1596
10.00	-0.2961					

Table 7

Ex. 2					
Component	**Time Points**	**R^2**	**Slope**	**k (min^{-1})**	**Half-life (t1/2), min**
NVP	0.25 - 8 min	0.973	-0.0265	0.0610	11.36
HEMA	0.25 - 4 min	0.998	-0.2810	0.6471	1.07
TEGDMA	0.25 - 4 min	0.963	-0.2951	0.6796	1.02
Norblock	0.25 - 4 min	0.993	-0.3568	0.8217	0.84
CGI 819	0.25 - 4 min	0.999	-0.5037	1.1600	0.60
OH-mPDMS	0.25 - 4 min	0.999	-0.2582	0.5946	1.17

Table 8

CE 2					
Component	**Time Points**	**R^2**	**Slope**	**k (min^{-1})**	**Half-life ($t_{1/2}$), min**
DMA	0.25 - 8 min	0.975	-0.1496	0.3445	2.01
HEMA	0.25 - 4 min	0.978	-0.2167	0.4991	1.39
TEGDMA	0.25 - 4 min	0.971	-0.2254	0.5191	1.34
Norblock	0.25 - 4 min	0.976	-0.1873	0.4314	1.61
CGI 819	0.25 - 4 min	0.981	-0.3088	0.7112	0.97
OH-mPDMS	0.25 - 4 min	0.988	-0.1814	0.4178	1.66

Table 9

Ex.#	2	CE2
Hydrophile (HP)	NVP	DMA
HP ½ life	11.36	2.01
Si ½ life	1.17	1.66
HP/Si	9.7	1.2
[μmol HP/μmol Si] @90% conversion of Si	55.25	9.27

[0183] In Example 2, the half-life of the NVP is nearly ten times slower (11.36 minutes) than the half-lives for the other monomers HEMA (1.07) and OH-mPDMS (1.17). In Comparative Example 1, the half-life of the DMA (2.01) is nearly the same as the half life of the silicone-containing component, OH-mPDMS (1.66). It is believed that the difference in wettability between the formulations of Example 1 and Comparative Example 1 is due to the substantially slower polymerization of the slow-reacting hydrophilic monomer in Example 1 (NVP) as compared to the hydrophilic monomer in Comparative Example 1 (DMA). Table 9 also shows that at 90% conversion of the silicone monomer, the molar ratio of the unreacted slow-reacting hydrophilic monomer NVP, compared to the unreacted silicone (mPDMS), is 55.25 for NVP, and only 9.27 for the DMA system. The NVP containing system displays improved wettability, as measured by contact angle, and increased oxygen permeability. The modulus of the DMA-containing formulation was substantially lower, which is believed to be an indication that the DMA and silicone monomers are more randomly incorporated in network. NVP system is believed to have larger blocks of silicone and NVP. Moreover the ratio of the kinetic half lives for the Comparative Example 2 system containing DMA as the hydrophile (1.21) is insufficient to provide a wettable lens. The ratio of molar concentrations of DMA and HO-PDMS for Comparative Example 1 was less than 10 (9.74).

Examples 3-5 and Comparative Example 3

[0184] The preparation described in Example 1 and kinetics evaluation described in Example 2 were repeated for the formulations listed in Table 10 below. The formulations for Example 2 and Comparative Example 2 are listed in Table 10 for convenience. Tables 11- 14 show a summary of the calculated kinetics data for Examples 3-5 and Comparative Example 3, and Table 15 shows the ratios of slow hydrophilic component to the silicone component. The kinetics data for Example 2 and Comparative Example 2 is shown in Tables 5 and 6, above.

Table 10

Comp.	Ex. 2	Ex. 3	CE2	CE 3	Ex. 4	Ex. 5
OH-mPDMS	40	40	40	40	0	0
SA2	0	0	0	0	41	40
NVP	50.5	50.5	0	0	51.5	50.5
DMA	0	0	50.5	50.5	0	0
HEMA	6.75	8.75	6.75	8.75	6.75	6.75
TEGDMA	0.5	0.5	0.5	0.5	0.5	0.5
Norblock	2	0	2	0	0	2
CGI 819	0.25	0.25	0.25	0.25	0.25	0.25

Table 11: Summary of Example 3 Kinetic Calculations

Component	**Time Points**	**R^2**	**Slope**	**k (min^{-1})**	**Half-life (t1/2), min**
NVP	0.25 - 4 min	0.869	-0.1133	0.2609	2.66
HEMA	0.25 - 8 min	0.869	-0.2911	0.6704	1.03
TEGDMA	0.25 - 4 min	0.998	-0.5114	1.1778	0.59
CGI 819	0.25 - 4 min	1.000	-0.5228	1.2040	0.58
OH-mPDMS	0.25 - 2 min	0.987	-0.3080	0.7093	0.98

Table 12: Summary of Comparative Example 3 Kinetics Calculations

Component	**Time Points**	**R^2**	**Slope**	**k (min^{-1})**	**Half-life (t1/2), min**
DMA	0.25 - 2 min	0.993	-0.1736	0.3998	1.73
HEMA	0.25 - 1 min	0.989	-0.3734	0.8599	0.81
TEGDMA	0.25 - 2 min	0.993	-0.5279	1.2158	0.57

(continued)

Component	Time Points	R^2	Slope	k (min^{-1})	Half-life (t1/2), min
CGI 819	0.25 - 2 min	0.991	-0.5106	1.1759	0.59
OH-mPDMS	0.25 - 1 min	0.987	-0.3262	0.7512	0.92

Table 13: Summary of Example 4 Kinetics Calculations

Component	Time Points	R^2	Slope	k (min^{-1})	lHalf-life (t1/2), min
NVP	0.25 - 1 min	0.944	-0.1839	0.4235	1.64
HEMA	0.25 - 2 min	0.970	-1.1455	2.6381	0.26
TEGDMA	0.25 - 2 min	0.942	-1.0470	2.411	0.29
CGI 819	0.25 - 4 min	0.959	-0.3555	0.8187	0.85
SA2	0.25 - 2 min	0.913	-0.7599	1.7500	0.40

Table 14: Summary of Example 5 Kinetics Calculations

Component	Time Points	R^2	Slope	k (min^{-1})	Half-life (t1/2), min
NVP	0.25 - 1 min	0.891	-0.0630	0.1451	4.78
HEMA	0.25 - 2 min	0.947	-1.2118	2.7908	0.25
TEGDMA	0.25 - 2 min	0.886	-2.1365	4.9204	0.14
Norbloc	0.25 - 2 min	0.981	-1.4710	3.3877	0.20
CGI 819	0.25 - 2 min	0.988	-0.4677	1.0771	0.64
SA2	0.25 - 2 min	0.712	-0.4544	1.0465	0.66

Table 15

Ex.#	2	3	CE2	CE3	4	5
Norbloc	Y	N	Y	N	N	Y
Hydrophile	NVP	NVP	DMA	DMA	NVP	NVP
HP ½ life	11.36	2.66	2.01	1.73	1.64	4.78
Silicone	HO-mPDMS	HO-mPDMS	HO-mPDMS	HO-mPDMS	SA2	SA2
Si ½ life	1.17	0.98	1.66	0.92	0.4	0.66
HP/Si	9.7	2.7	1.2	1.88	4.1	7.24
[μmol HP/μmol Si] @90% conversion	55.25	40.21	9.27	8.99	55.79	60.23

[0185] Considering the data in Table 15, including a UV absorbing compound in a photoinitiated reactive monomer mixture causes the half life of the slow-reacting hydrophilic monomer NVP to increase by between 60 and 400%, while the half life of DMA increases marginally from 1.73 to 2.01 (16%). The half life of the HO-mPDMS was also increased. The half life of the SA2 silicone decreased upon addition of the UV absorber, Norbloc, but the decrease was not enough to offset the substantial increase in the half life of the NVP. Comparing Comparative Example 2 (formulation containing DMA and Norbloc) to Comparative Example 3 (formulation containing DMA without Norbloc), it can be seen that the inclusion of Norbloc in a DMA-containing formulation slowed the reaction rate for the crosslinker TEGDMA and more than doubled its half life. In the DMA/Norbloc-containing formulation, this meant that the crosslinker had a reactivity rate much more similar to the hydrophilic monomer and silicone-containing component. Even though the inclusion of a UV absorber such as Norbloc slowed the reaction rate for TEGDMA, it was still faster (4.92) than both the hydrophilic monomer (0.145) and silicone-containing component (1.05).

[0186] Contact lenses were made from the Formulations of Examples 3-5 and Comparative Example 3 using the method described in Example 2. The properties of the lenses were measured and are shown in Table 16, below.

Table 16

Ex. #	% H_2O	% Haze	DCA	Mechanicals		Dk
				Mod. (psi)	Elong. (%)	
2	58.4 (0.2)	4 (0)	44 (4)	103 (11)	220 (36)	75
3	66.6 (0.1)	24 (1)	50 (3)	63 (8)	192 (76)	79
CE2	59.8 (0.1)	5 (1)	127 (14)	54 (7)	227 (52)	49
CE3	58.1 (0.2)	3 (1)	132 (7)	78 (7)	199 (39)	49
4	67 (0.2)	67 (2)	51 (3)	64 (7)	229 (97)	82
5	65.5 (0.1)	8 (1)	68 (7)	105 (9)	242 (49)	57

[0187] The lenses of Examples 2 through 5 show desirable haze and wettability, as well as a balance of other desirable properties. Each of these Examples had ratios of the slow-reacting hydrophilic monomer half life: silicone-containing component half life greater than about 2. Comparative Examples 2 and 3 had half life ratios of below 2 (1.2 and 1.88 respectively). Thus, half life ratios greater than about 2, and in some embodiments greater than about 3 are desirable to provide desirable wettability.

[0188] Comparing the modulii of Comparative Example 2 (54 psi, with Norbloc) and Comparative Example 3 (78 psi without Norbloc) it can be seen that the change in the reactivity rate for TEGDMA caused by the inclusion of Norbloc was sufficient to decrease crosslinking in the network of the resulting polymer. Thus, in additional to changing the amount of crosslinker, one can also choose a crosslinker with a different reactivity ratio to achieve a desired polymer structure and modulus. The same behavior is also observed comparing the SA2/NVP-containing formulations of Examples 4 and 5.

Examples 6 -10

[0189] The level of BHT and initiator was varied as shown in Table 17. In Example 10 2 wt% VINAL, was added to the formulation of Example 6.

Table 17

Ex#	**6**	**7**	**8**	**9**	**10**
[BHT] ug/g	1429	166	166	166	1429
mPDMS 1000	15	15	15	15	15
OH-mPDMS, n=4	25	25	25	25	25
NVP	50.5	50.5	50.38	50.25	48.5
HEMA	6.75	6.75	6.75	6.75	6.54
VINAL	0	0	0	0	2
TEGDMA	0.5	0.5	0.5	0.5	0.5
Norbloc	2	2	2	2	2
CGI 819	0.25	0.25	0.37	0.5	0.25

[0190] The kinetics for the two formulations were measured and calculated as described in Example 1, and contact lenses were made as described in Example 2. The kinetics for the formulations are shown in Tables 18-24, and the lens properties are shown in Table 25.

Table 18: Example 6

Component	Time Points	R^2	Slope	k (min^{-1})	Half-life (t1/2), min
NVP	0.25 - 8 min	0.975	-0.0267	0.0615	11.27
HEMA	0.25 - 4 min	0.993	-0.2044	0.4707	1.47
TEGDMA	0.25 - 2 min	0.947	-0.3171	0.7303	0.95
Norblock	0.25 - 4 min	0.999	-0.2441	0.5622	1.23
CGI 819	0.25 - 4 min	1.000	-0.5438	1.2524	0.55
OH-mPDMS	0.25 - 4 min	0.997	-0.1885	0.4341	1.60
mPDMS 1000	0.25 - 4 min	0.997	-0.1515	0.3489	1.99

Table 19: Example 7

Component	Time Points	R^2	Slope	k (min^{-1})	Half-life (t1/2), min
NVP	0.25 - 8 min	0.989	-0.0294	0.0677	10.24
HEMA	0.25 - 4 min	0.997	-0.2527	0.5820	1.19
TEGDMA	0.25 - 2 min	0.989	-0.4923	1.1338	0.61
Norblock	0.25 - 4 min	0.999	-0.3536	0.8143	0.85
CGI 819	0.25 - 4 min	1.000	-0.5228	1.2040	0.58
OH-mPDMS	0.25 - 4 min	0.999	-0.2499	0.5755	1.20
mPDMS 1000	0.25 - 2 min	0.996	-0.1474	0.3395	2.04

Table 20: Example 8

Component	Time Points	R^2	Slope	k (min^{-1})	Half-life (t1/2), min
NVP	0.25 - 8 min	0.990	-0.0381	0.0877	7.90
HEMA	0.25 - 4 min	0.985	-0.3395	0.7819	0.89
TEGDMA	0.25 - 4 min	0.946	-0.3549	0.8173	0.85
Norblock	0.25 - 4 min	0.980	-0.5042	1.1612	0.60
CGI 819	0.25 - 4 min	0.999	-0.4793	1.1038	0.63
OH-mPDMS	0.25 - 4 min	0.989	-0.3222	0.7420	0.93
mPDMS 1000	0.25 - 4 min	0.993	-0.2765	0.6368	1.09

Table 21: Example 9

Component	Time Points	R^2	Slope	k (min^{-1})	Half-life (t1/2), min
NVP	0.25 - 8 min	0.887	-0.0611	0.1407	4.92
HEMA	0.25 - 4 min	0.924	-0.4627	1.0656	0.65
TEGDMA	0.25 - 4 min	0.852	-0.4986	1.1483	0.60
Norblock	0.25 - 4 min	0.985	-0.6741	1.5525	0.45
CGI 819	0.25 - 4 min	1.000	-0.4326	0.99628	0.70
OH-mPDMS	0.25 - 4 min	0.940	-0.4831	1.1126	0.62
mPDMS 1000	0.25 - 4 min	0.989	-0.4703	1.0831	0.64

Table 22: Example 10

Component	**Time Points**	**R^2**	**Slope**	**k (min^{-1})**	**Half-life (t1/2), min**
VINAL	0.25 - 18 min	0.904	-0.0126	0.0290	23.88
NVP	0.25 - 8 min	0.949	-0.0273	0.0629	11.02
HEMA	0.25 - 2 min	0.979	-0.3082	0.7098	0.98
TEGDMA	0.25 - 2 min	0.984	-0.4253	0.9795	0.71
Norbloc	0.25 - 2 min	0.975	-0.2924	0.6734	1.03
CGI 819	0.25 - 4 min	1.000	-0.4882	1.1243	0.62
OH-mPDMS	0.25 - 2 min	0.971	-0.2819	0.6492	1.07
mPDMS 1000	Not Measured				

Table 23

Ex.#	6	7	8	9	10
[BHT] **ug/g**	9324	901	901	901	9324
[CGI 819]	0.25	0.25	0.37	0.5	0.25
NVP ½ life	11.27	10.24	7.90	4.92	11.02
mPDMS ½ life	1.99	2.04	1.09	0.64	**
OH-mPDMS ½ life	1.60	1.02	0.93	0.62	1.07
NVP/MPDMS	5.7	5.0	7.3	7.7	**
NVP/OH-mPDMS	7.0	8.5	8.5	7.9	10.3
VINAL/HO-PDMS	**	**	**	**	22.3
[μmol NVP]/[μmol mPDMS] @90% conversion	211.45	233.18	273.5	251.9	XX
[μmol NVP]/[μmol HO-mPDMS] @90% conversion	94.71	83.6	92	99	68.57
** Not applicable XX not measured.					

Table 24

Ex. #	**6**	**7**	**8**	**9**	**10**
% H_2O	59.1 (0.1)	60.0 (0.2)	61.3(0.2)	63.6(0.2)	61.3 (0.2)
% Haze	3 (1)	5 (1)	4 (1)	5 (0)	NT
DCA	49 (2)	47 (3)	52 (4)	56 (5)	51 (3)
Mod. (psi)	92 (10)	84 (10)	65 (9)	66 (7)	84 (12)
Elong. (%)	188 (67)	194 (64)	197 (25)	163 (61)	149(61)
Dk	86.7	90.7	82.8	82.3	90.4
Lipocalin (μg/lens)	3.16 (0.6)	3.37 (0.2)	NT	NT	2.98 (0.3)
Total lipids (μg/lens)	22.7 (2.9)	23 (1.9)	NT	NT	13.2 (1.9)
Lysozyme (μg/Lens)	5.6 (0.9)	NT	NT	NT	39 (6.2)
Lysozyme Activity (%)	68 (2.7)	NT	NT	NT	78.7 (2.5)
PQ1 Uptake (μg/mL)	7.4 (0.4)	NT	NT	NT	7.1 (0.1)

[0191] All the lenses of Examples 6-10 have half life ratios greater than about 5, and all display desirably low contact angles (less than 60°), very low haze (less than 10) and desirable oxygen permeabilities greater than 80. The lenses of Examples 6-10 also have concentration ratios of the slow-reacting hydrophilic monomer to the silicone-containing components at 90% conversion of greater than about 83. Comparing Examples 6 and 7 shows that decreasing the inhibitor concentration from 1429 μg/g to 166 μg/g reduces the modulus slightly, but has a negligible impact on the other measured lens properties. Comparing Examples 7-9, decreases both the modulus and the Dk and increases the water content of the resultant lenses, particularly comparing Examples 7 and 9. This would suggest that the incorporation of the HO-PDMS is having a larger effect on the Dk than the incorporation of the mPDMS, as the kinetic ratio of NVP to HO-PDMS is trending in the same direction as the Dk for Examples 7-9.

[0192] Example 10 contained 2 wt% of VINAL, an ionic amide containing vinyl ether. The kinetics data in Table 23 confirms that VINAL is a slow reacting monomer. The lenses of Example 10 displayed greatly improved lysozyme uptake (39 μg/lens) compared to Example 6 (5.6 μg/lens), which contained no VINAL. The lens of Example 10 also displayed PQ-1 uptake which was no different than Example 6. PQ-1 is a cationic preservative which is present in a number of cleaning and care solutions. Contact lenses with blocks of anionic repeating units, or contact lenses with coatings of anionic polymers, can display markedly increased PQ-1 uptake values. The low value for Example 10 indicates that the VINAL was generally randomly polymerized with the NVP.

Examples 11-17

[0193] A series of lens formulations were formed from the following reactive components:

38.5 wt% mPDMS
NVP
hydroxyalkyl methacrylate, shown in Table 25
1 wt % TEGDMA
0.25 CGI 819

[0194] The amount of hydroxylalkyl (meth)acrylate and NVP were varied to provide molar ratios of the hydroxylalkyl (meth)acrylate:NVP of about 0.2. GMMA has two hydroxyl groups. Accordingly, formulations having two different concentrations of GMMA were prepared, Example 16 (13.23 wt% GMMA, 0.408 ratio, counting both hydroxyls) and Example 17 (6.62 wt % GMMA, 0.204, counting two hydroxyl).

[0195] The reactive components were mixed with a diluent (50% TAA/50% DA) in a ratio of 80 wt% reactive components: 20 wt% diluent. Examples 15 and 16 produce hazy reaction mixtures which were not cured into lenses. Examples 11-14 and 17 produced clear reaction mixtures which were cast into lenses using the following the procedure. The reaction mixture was degassed by applying vacuum at ambient temperature for about 17(±3) minutes. The reaction mixture was then dosed into thermoplastic contact lens molds (front curves made from Zeonor, and back curves from polypropylene), The BC was placed on the FC mold to produce 8 BC/FC assemblies in a pallet. Pallets were placed on a mirrored surface and a quartz plate (12.50 mm x 6.25 mm x 0.50 mm) was placed over each pallet. The lenses were cured for about 15 minutes at 45°C, under a nitrogen atmosphere, using Philips TL 20W/03T fluorescent bulbs and 4-5 mW/cm^2.

[0196] Lenses were released in 50/50 IPA/water, extracted in 70/30 IPA/water and subsequently equilibrated in deionized water. Lenses were transferred into vials containing borate buffered saline for at least 24 hours and then autoclaved at 122°C for 30 minutes. Lens properties were measured and are reported in Table 63, below.

Table 25

Example	11	12	13	14	15	16	17
Component	**HEMA**	**HPMA**	**HBMA**	**DMHEMA**	**HEAA**	**GMMA**	**GMMA**
[NVP] wt %	47.5	47.5	45.18	45.18	48.75	45.01	51.63
[HOMA] wt%	10.75	10.75	13.07	13.07	9.50	13.23	6.62
HOMA:NVP (molar)	0.193	0.174	0.203	0.203	0.188	0.408	0.204
% H_2O	59.1 (0)	58.9 (0.1)	54.5	60.4	NT*	NT	62.6
% Haze	8 (0)	16 (0)	8	15	NT*	NT*	12
DCA	60 (7)	63 (5)	46	70	NT*	NT*	49
MOD (psi)	79.9 (1.9)	73.4 (1.4)	120.5	68.7	NT*	NT*	70.4

(continued)

Example	11	12	13	14	15	16	17
Component	**HEMA**	**HPMA**	**HBMA**	**DMHEMA**	**HEAA**	**GMMA**	**GMMA**
Elong (%)	196.2 (24.6)	230.1 (1.8)	179.3	206.5	NT*	NT*	203.5
Dk	89.1	93.4	93.4	90	NT*	NT*	85.3
NT* = Not Tested							

[0197] Comparing Examples 16 and 17, it can be seen that when the molar amount of GMMA was adjusted to account for both hydroxyls, clear lenses were formed. It is believed that Example 15, which included HEAA as the hydroxyalkyl (meth)acrylate, did not provide wettable lenses because the HEAA contains two polar groups, the amide and hydroxyl groups, making the HEAA more polar than the other hydroxylalkyl (meth)acrylates used in Examples 11-14 and 16-17. It is believed that the increased polarity of HEAA caused compatibility issues with the mPDMS. However, HEAA has the potential to work with more polar silicones, such as SiMAA, OH-mPDMS, N-(2,3-dihydroxypropane)-N'-(propyl tetra(dimethylsiloxy) dimethylbutylsilane)acrylamide. Thus, a variety of hydroxylalkyl (meth)acrylate compounds can be used to form the hydrogels of the present invention.

Examples 18-21

[0198] Additional reaction mixtures were made varying the diluents system used and the siloxane components as shown in Tables 64 and 65, below. All mixtures were formed using 80wt% reactive components and 20wt% diluents. The lenses were molded, cured, processed and sterilized according to the procedure described in Example 27, above. The lens properties were measured and are shown in Tables 26 and 27.

Table 26

	Ex 18	Ex 19	Ex 20	Ex 21
mPDMS	20	20	20	20
TRIS	18.5	18.5	18.5	18.5
NVP	47.5	47.5	47.5	47.5
HEMA	10.75	10.75	10.75	10.75
TEGDMA	1	1	1	1
Norbloc	2	2	2	2
CGI819	0.25	0.25	0.25	0.25
Diluent	1:1 EtOAc: EtOH	TAA	D30	1:1 TAA:DA
EWC	46.0 ± 1.6%	55.5 ± 0.1%	58.9 ± 0.1%	57.4 ± 0.1%
Haze	50 ± 19	10 ± 2	12 ± 1	7 ± 0
DCA	NT	NT	66 ± 4°	69 ± 6°
Modulus	100 ± 13 psi	83 ± 9 psi	80 ± 7 psi	88 ± 6 psi
Elongation	305 ± 105%	330 ± 49%	307 ± 39%	285 ± 73%
Dk	NT	80	64	75
NT=Not tested				

Table 27

	Ex22**	Ex 23	Ex 24**	Ex 25
mPDMS	38.5	38.5	38.5	38.5
NVP	47.5	47.5	47.5	47.5

(continued)

	Ex22**	Ex 23	Ex 24**	Ex 25
HEMA	10.75	10.75	10.75	10.75
TEGDMA	1	1	1	1
Norbloc	2	2	2	2
CGI819	0.25	0.25	0.25	0.25
diluent	1:1 EtOAc:EtOH	TAA	D30	1:1 TAA:DA
EWC	**	56.3 ± 0.2%	**	59 ± 0.1%
Haze	**	8 ± 0	**	9 ± 1
DCA	**	74 ± 2°	**	54 ± 3°
Modulus	**	62 ± 9 psi	**	70 ± 5 psi
%Elongation	**	252 ± 63%	**	245 ± 62%
Dk	**	107	**	91
***Blends were immiscible*				

[0199] The blends of Examples 22 and 24 were immiscible and were not cast into lenses. These Examples show that a wide range of diluents may be used to form the lenses of the present invention. These examples also show that secondary alcohols provide formulations with a desirable balance of properties, including clarity and modulus, when photocured.

Examples 26-31

[0200] Lenses were made from the formulations in Table 28 with concentration of the reactive components, adding up to 100 wt%. No diluent was used.

[0201] The reaction mixtures were degassed by applying vacuum at ambient temperature for about 17(±3) minutes. The reaction mixture (75 μL) was then dosed at room temperature and <0.1% O_2, into thermoplastic contact lens molds (FC - Zeonor, BC Polypropylene) which had been degassed in N_2 box at RT (Compartment 1, Figure 1) for a minimum of 12 hours prior to dosing. The BC was placed on the FC mold and the lenses were moved into Compartment 2 and cured for 20 minutes, at an intensity of 4 - 5 mW/cm^2, <0.1% O_2, and 62 - 65°C.

[0202] The molds for all the lenses were mechanically separated and the lenses remained in the FC. The lenses were dry released by pressing on the back of the front curve. Lenses were extracted in DI water

All lenses were stored in borate buffered packing solution in lens vials and sterilized at 122°C for 30 minutes.

[0203] The ability of the lenses to recover from mechanical stress, such as folding was evaluated. A crease was generated in each lens by placing a folded unsterilized lens between two rectangular glass plates (12.5 cm x 6.3 cm x 0.5 cm (~113 g)) for five minutes. The lens was subsequently sterilized and visually inspected using a DL2 (17.5X) and Optimec, to discern the level of recovery. • Increasing degrees of creasing/stress were created in unsterilized lenses by using 2, 3, 4 or 5 top plates. The results of the stress test are shown in Table 30.

[0204] The stress test values for three commercial lenses, ACUVUE OASYS with HYDRACLEAR Plus, Biofinity and Clariti lenses are shown as controls.

[0205] The properties of the lenses were measured and are shown in Table 29.

Table 28

Ex.#	**26**	**27**	**28**	**29**	**30**	**31**
mPDMS 1000	19.35	19.35	19.35	19.35	19.35	19.35
OH-mPDMS (n=4)	27.50	27.50	27.50	27.50	27.50	27.50
VMA	0.00	8.00	12.00	22.00	32.00	44.00
HEMA	6.50	6.50	6.50	6.50	6.50	6.50
NVP	44.00	36.00	32.00	22.00	12.00	0.00

(continued)

Ex.#	26	27	28	29	30	31
TEGDMA	0.20	0.20	0.20	0.20	0.20	0.20
TAC	0.20	0.20	0.20	0.20	0.20	0.20
Norbloc	1.75	1.75	1.75	1.75	1.75	1.75
CGI 819	0.50	0.50	0.50	0.50	0.50	0.50
Diluent	0.00	0.00	0.00	0.00	0.00	0.00

Table 29

Lens	% H_2O	% Haze	DCA	Mechanicals		Dk	Res. NVP	Res. VMA
				Mod. (psi)	Elong. (%)			
26	55 (0)	6 (0)	55 (3)	95 (6)	270 (34)	96	0.8 (0.02)	N/A
27	56 (0)	6 (0)	67 (5)	104 (7)	233 (49)	100	NT	NT
28	56 (0)	5 (0)	58 (4)	100 (8)	258 (36)	100	0.51 (0.02)	1.15 (0.08)
29	58 (0)	6 (0)	56 (9)	91 (9)	223 (54)	96	0.4 (0.04)	2.2 (0.2)
30	58 (0)	7 (0)	56 (5)	92 (10)	260 (62)	103	0.3 (0.01)	2.98 (0.06)
31	58 (0)	13 (2)	50 (10)	86 (7)	262 (54)	106	N/A	4.52 (0.61)

Table 30

Post Sterilization Inspection - DL2 (17.5X) and Optimec						
Ex#	Control (0 Plate)	1 Plate	2 Plates	3 Plates	4 Plates	5 Plates
26	G	G	G	G	G	G
27	G	G	G	G	G	G
28	G	G	G	G	G	G
28	G	G	G	G	G	G
30	G	G	G	G	G	G
31	G	G	G	G	G	G

Examples 32-34

[0206] Reactive mixtures were formed from the components listed in Table 31 and degassed by applying vacuum at ambient temperature for about 17(±3) minutes. The reaction mixture (75 μL) was then dosed at room temperature and <0.1% O_2, into thermoplastic contact lens molds (FC - Zeonor, BC Polypropylene) which had been degassed in N_2 box at RT (Compartment 1, Figure 1) for a minimum of 12 hours prior to dosing. The BC was placed on the FC mold to produce 8 BC/FC assemblies in a pallet. Eight pallets were prepared, moved into the cure compartment (Compartment 2) and placed on a mirrored surface. A quartz plate (12.50 mm x 6.25 mm x 0.50 mm) was placed over each pallet and the lenses were and cured for 20 minutes, at an intensity of 4 - 5 mW/cm^2, <0.1% O_2, and 62-65°C.

[0207] The molds for all the lenses were manually demolded (lenses remained in FC). Lenses were released in 50/50 IPA/water, extracted in 50/50 IPA/water and subsequently equilibrated in de-ionized water. Lenses were transferred into vials containing borate buffered saline for at least 24 hours and then autoclaved for 1, 3, 6 and 9 cycles at 122°C for 30 minutes. Water content and modulus were measured after each sterilization cycle.

[0208] The resulting lenses were very clear, and felt lubricious when rubbed between the thumb and forefinger.

Table 31

Component	E. 32	33	34
Tris	19.10	19.10	19.10
OH-mPDMS	25.00	25.00	25.00
NVP	46.50	44.00	45.15
HEMA	6.75	6.75	6.75
TEGDMA	0.20	0.20	0.20
TAC	0.20	0.20	0.20
Norbloc	1.75	1.75	1.75
VINAL	0.00	2.50	0.00
MAA	0.00	0.00	1.35
CGI 819	0.50	0.50	0.50
Diluent	0.00	0.00	0.00
TAM	100.00	100.00	100.00

Synthetic Preparation 1: 2-hydroxybutyl methacrylate (HBMA)

[0209] A blend of 72 grams 1,2-epoxybutane (Aldrich), 0.85 g 4-methoxyphenol (Aldrich), and 6.5 g potassium hydroxide was stirred in a 500 ml round bottomed flask equipped with an addition funnel and thermocouple thermometer. 172 g methacrylic acid was added via the addition funnel, and the blend was slowly to 75°C, and stirred overnight under an air, then increased to 88°C for 4 hours. The mixture was cooled, and 700 ml of 2.0 N NaOH was added to the mixture in a separatory funnel. The upper layer was washed with borate buffered saline three times. Ethyl ether (200 ml) was added to the combined saline washes to extract any product. The combined organic layers were dried over $NaSO_4$. The $NaSO_4$ was filtered out and the product was distilled (90-98°C/~4 mm Hg). 17.5 g product was collected, to which was added 4 mg 4-methoxyphenol. ^1H NMR: 6.1 ppm (1H, m), 5.5 (1H, m), 4.8 (0.25H m), 4.2 (0.64 H, dd, 8.1 and 11.7 Hz), 4.0 (0.64 Hz, dd, 6.9 and 11.4 Hz), 3.6-3.8 1.26H, m), 2.3 (OH, br s), 1.9 (3 H, m), 1.4-1.7 (2 H, m), 0.9 (3H, m); consistent with a blend of 2-hydroxy-1-propylmethacrylate and 1-hydroxy-2-propylmethacrylate.

Synthetic Preparation 2: dimethylhydroxyethylmethacrylate

[0210] The same procedure as for HBMA was used, but substituting 1,2-epoxy-2-methylpropane for the 1,2-epoxypropane. The product was isolated by distillation at 47-48°/0.4-0.6 mm Hg.. ^1H NMR: 6.1 ppm (1H, s), 5.5 (1H, m), 4.0 (2H, s), 2.1 (OH, br s), 1.9 (3 H, s), 1.2 (6 H, m); consistent 2-hydroxy-2-methyl propylmethacrylate (dimethylhydroxyethylmethacrylate).

Synthetic Preparation 3: VINAL

[0211] 4.82 g vinyl chloroformate was added to a mixture of 8.19 g β-alanine (Aldrich) in 74 ml acetonitrile. The resulting mixture was refluxed for 2 hours, then cooled to room temperature and allowed to sit for 2 hours. It was filtered and solvent was removed under reduced pressure. The crude product was dissolved in 30 ml distilled water and washed three times with ethyl acetate. The combined ethyl acetate washes were washed with 50 ml deionized water. Solvent was evaporated from the combined ethyl acetate washes to yield 4.5 g product as a fluffy yellowish solid. ^1H NMR: 7.1 ppm (dd, 1H), 5.4 ppm (br s, OH), 4.7 ppm (dd, 1H), 4.4 ppm (dd, 1H), 3.5 ppm (q, 2H), 2.6 ppm (t, 2H).

Claims

1. A silicone hydrogel formed from a reaction mixture comprising:
30 to 75 wt% of a mixture of slow-reacting hydrophilic monomers, each having a slow-reacting hydrophilic monomer kinetic half life, said mixture of slow reacting hydrophilic monomers comprising at least one slow-reacting anionic monomer comprising at least one anionic group selected from carboxylic acids, sulfonic acids and their salts and

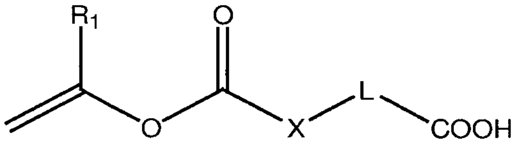
mixtures thereof;

at least one silicone-containing component having a silicone-containing component kinetic half life, which may be optionally substituted with at least one hydroxyl containing group; and
at least one hydroxyl-containing component selected from said silicone-containing component substituted with at least one hydroxyl containing group, at least one hydroxyalkyl monomer, and mixtures thereof,
wherein the ratio of each of said slow-reacting hydrophilic component half lives to said silicone-containing component half life is at least 2.

2. The silicone hydrogel of claim 1 wherein the reaction mixture comprises;
37 to 75 wt%; or
37 to 70 wt%; or
39 to 60 wt%, of at least one slow-reacting hydrophilic monomer having a slow-reacting hydrophilic monomer kinetic half life.

3. The silicone hydrogel of any preceding claim
wherein said slow-reacting anionic component comprises reactive functionality selected from the group consisting of methacrylamide reactive groups, N-vinyl amides, O-vinyl carbamates, O-vinyl carbonates, N-vinyl carbamates, O-vinyl ethers, O-2-propenyl, wherein the vinyl or allyl groups may be further substituted with a methyl group.

4. The silicone hydrogel of any preceding claim wherein said slow-reacting anionic component is selected from the group consisting of 4-acrylamidobutanoic acid (ACAII),3-acrylamidopropionic acid, 5-acrylamidopentanoic acid, 3-acrylamido-3-methylbutanoic acid (AMBA), N-vinyloxycarbonyl-a-alanine, N-vinyloxycarbonyl-β-alanine (VINAL), vinyl sulphonate salt; acetic acid, 2-carboxymethoxy)-,1-ethenylester, of Formula



Formula Q

Where R_1 is H or methyl, X is O or NR_{16}, R_{16} is H or C_{1-3} alkyl), and L is divalent C_{1-4} alkyl group; and mixtures thereof, optionally
wherein said slow-reacting anionic component is selected from the group consisting of N-vinyloxycarbonyl-α-alanine; N-vinyloxycarbonyl-β-alanine (VINAL); vinyl sulphonate sodium salt; acetic acid, 2-carboxymethoxy)-,1-ethenylesters of Formula Q, mixtures thereof and the like.

5. The silicone hydrogel of any of claims 1 - 3 wherein said slow-reacting anionic component is present in the reactive mixture in an amount below 20 mole%.

6. The silicone hydrogel of any of claims 1 - 3 wherein said slow-reacting anionic component is present in the reactive mixture in an amount between:

i) 0.5 and 15 mole %; or
ii) 0.5 and 5 mole % ; or
iii) 0.5 and 10 mole %,

based upon all components in the reaction mixture.

7. The silicone hydrogel of claim any preceding claim wherein all of said slow-reacting components have the same reactive functionality, optionally wherein all of said slow-reacting components have vinyl functionality.

8. The silicone hydrogel of claim any preceding claim wherein said reaction mixture further comprises at least one slow reacting crosslinker and at least one fast reacting crosslinker.

9. The silicone hydrogel of claim 8 wherein said slow reacting crosslinkers have only vinyl reactive functionality and

said fast reacting crosslinkers have (meth)acrylate reactive functionality only, optionally
wherein said slow reacting crosslinker comprises triallylcyanurate (TAC) and said fast reacting crosslinker is selected from the group consisting of ethylene glycol dimethylacrylate (EGDMA), tetraethyleneglycol dimethacrylate (TEGDMA) and mixtures thereof.

10. The silicone hydrogel of claims 7 or 8 wherein said at least one slow reacting crosslinker and at least one fast reacting crosslinker are each present in said reaction mixture in amounts between:

i) 0.4 to 2.0 mmoles per 100 g of reactive components; or
ii)0.3 to about 2.0 mmol/100 g of polymerizable components.

11. The silicone hydrogel of any preceding claim wherein said reactive mixture further comprises at least one reactive cationic component, optionally
wherein said cationic component or hydrogen bonding component is present in an amount sufficient to improve surface resilience of said hydrogel.

12. The silicone hydrogel of claim 11 wherein said at least one reactive cationic component has the same reactive functionality as at least one of said silicone containing components.

13. The silicone hydrogel of any preceding claim wherein said kinetic half life ratio is at least 3.

14. The silicone hydrogel of any preceding claim further comprising a Dk of:

i) at least 80 barrers; or
ii) at least 85 barrers, wherein Dk is measured according to the method described in the "Oxygen Permeability (Dk)" section of the detailed description.

15. The silicone hydrogel of any preceding claim further comprising a %haze of:

i) less than 70%; or
ii) less than 50%, wherein %haze is measured according to the method described in the "Haze Measurement" section of the "Haze Solubility Parameter" of the detailed description.

16. The silicone hydrogel of any preceding claim further comprising a water content of:

i) at least 55%; or
ii) at least 60%.

17. The silicone hydrogel of any preceding claim further comprising a modulus of:

i) less than 150 psi; or
ii) 100 psi or less, wherein modulus is measured according to the method described "Modulus" section of the detailed description.

18. The silicone hydrogel of any preceding claim wherein said reaction mixture further comprises at least one UV absorbing compound.

19. The silicone hydrogel of claim 18 wherein said at least one UV absorbing compound is reactive.

20. The silicone hydrogel of claim 19 wherein said at least one UV absorbing compound is selected from:

i) benzotriazoles; or
ii) the group consisting of reactive 2-(2'-hydroxyphenyl)benzotriazoles, 2-hydroxybenzophenones, 2-hydroxyphenyltriazines, oxanilides, cyanoacrylates, salicylates and 4-hydroxybenzoates; or
iii) the group consisting of 2-(2'-hydroxy-5-methacrylyloxyethylphenyl)-2H-benzotriazole, 5-vinyl and 5-isopropenyl derivatives of 2-(2,4-dihydroxyphenyl)-2H-benzotriazole and 4-acrylates or 4-methacrylates of 2-(2,4-dihydroxyphenyl)-2H-benzotriazole or 2-(2,4-dihydroxyphenyl)-1,3-2H-dibenzotriazole, and mixtures thereof.

21. The silicone hydrogel of claim 19 comprising between:

i) 0.5 and 4 wt.%, of at least one UV absorber; or
ii) 1 wt% and 2 wt% UV absorber.

22. The silicone hydrogel of any preceding claim wherein said reaction mixture is free of diluent, and/or wherein said reaction mixture is free of 3-methacryloxypropyltris(trimethylsiloxy)silane (TRIS).

23. The silicone hydrogel of any preceding claim wherein i) said slow-reacting hydrophilic monomer comprises a reactive group selected from the group consisting of (meth)acrylamides, vinyls, allyls and combinations thereof and said silicone-containing component comprises a reactive group selected from the group consisting of (meth)acrylates, styryls, amides and mixtures thereof, and/or
ii) said slow-reacting hydrophilic monomer comprises a reactive group selected from the group consisting of vinyls, allyls and combinations thereof and said silicone-containing component comprises a reactive group selected from the group consisting of (meth)acrylates, styryls, amides and mixtures thereof.

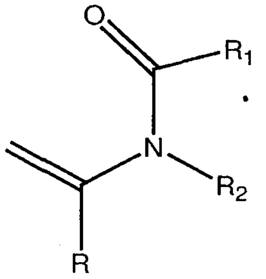
24. The silicone hydrogel of any preceding claim wherein said slow-reacting hydrophilic monomer is present in an amount between:

i) 39 and 70wt%; or
ii) 39 and 60 wt%.

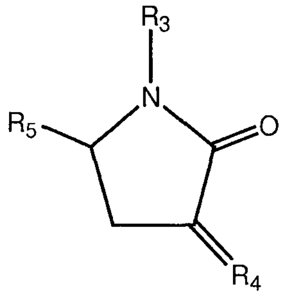
25. The silicone hydrogel of any preceding claim

i) wherein said slow-reacting hydrophilic monomer comprises a reactive group selected from the group consisting of N-vinyl amides, O-vinyl carbamates, O-vinyl carbonates, N-vinyl carbamates, O-vinyl ethers, O-2-propenyl, wherein the vinyl or allyl groups may be further substituted with a methyl group; and/or
ii) wherein said slow reacting hydrophilic monomer comprises at least one hydrophilic group selected from the group consisting of hydroxyls, amines, ethers, amides, ammonium groups, carboxylic acid, carbamates and combinations thereof; and/or
iii) wherein said slow reacting hydrophilic monomer comprises at least one hydrophilic group selected from the group consisting of hydroxyls, ethers, amides, carboxylic acid combinations thereof.

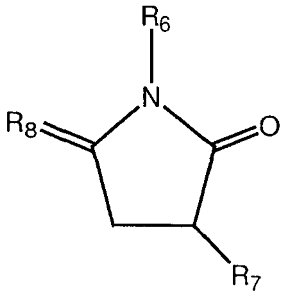
26. The silicone hydrogel of claim 1 wherein said slow reacting hydrophilic monomer is selected from N-vinylamide monomer of Formula I, a vinyl pyrrolidone of Formula II-IV, n-vinyl piperidone of Formula V:



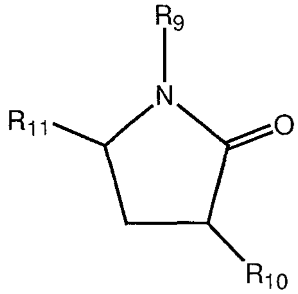
Formula I



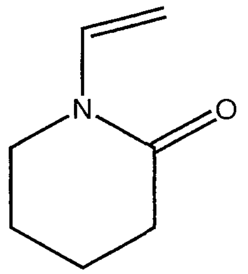
Formula II



Formula III



Formula IV



Formula V

wherein R is H or methyl;
R_1, R_2, R_3, R_6, R_7, R_{10}, and R_{11} are independently selected from H, CH_3, CH_2CH_3, $CH_2CH_2CH_3$, $C(CH_3)_2$;
R_4 and R_8 are independently selected from CH_2, CHCH3 and $C(CH_3)$;
R_5 is selected from H, methyl, ethyl; and
R_9 is selected from $CH=CH_2$, $CCH_3=CH_2$, and $CH=CHCH_3$.

27. The silicone hydrogel of claim 26 wherein:

i) the slow-reacting hydrophilic monomer is selected from the vinyl pyrrolidone of Formula II or IV or the N-vinyl amide monomer of Formula I, and the total number of carbon atoms in R_1 and R_2 is 4 or less; or

ii) the slow-reacting hydrophilic monomer is selected from a vinyl pyrrolidone of Formula III or IV and R_6 is methyl, R_7 is hydrogen, R_9 is $CH=CH_2$, R_{10} and R_{11} are H; or

iii) the slow-reacting hydrophilic monomer is selected from ethylene glycol vinyl ether (EGVE), di(ethylene glycol) vinyl ether (DEGVE), N-vinyl pyrrolidone (NVP), 1-methyl-3-methylene-2-pyrrolidone, 1-methyl-5-methylene-2-pyrrolidone, 5-methyl-3-methylene-2-pyrrolidone; 1-ethyl-5-methylene-2-pyrrolidone, N-methyl-3-methylene-2-pyrrolidone, 5-ethyl-3-methylene-2-pyrrolidone, 1-n-propyl-3-methylene-2-pyrrolidone, 1-n-propyl-5-methylene-2-pyrrolidone, 1-isopropyl-3-methylene-2-pyrrolidone, 1-isopropyl-5-methylene-2-pyrrolidone, N-vinyl-N-methyl acetamide (VMA), N-vinyl-N-ethyl acetamide, N-vinyl-N-ethyl formamide, N-vinyl formamide, N-vinyl acetamide, N-vinyl isopropylamide, allyl alcohol, N-vinyl caprolactam, N-2-hydroxyethyl vinyl carbamate, N-carboxy-β-alanine N-vinyl ester; N-carboxyvinyl-β-alanine (VINAL), N-carboxyvinyl-α-alanine and mixtures thereof; or

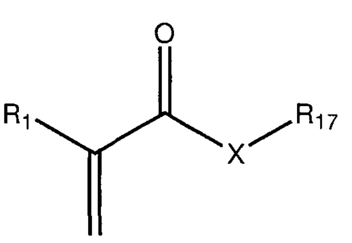
iii) wherein the slow-reacting hydrophilic monomer is selected from NVP, VMA and 1-methyl-5-methylene-2-pyrrolidone; or

iv) wherein the slow-reacting hydrophilic monomer comprises NVP.

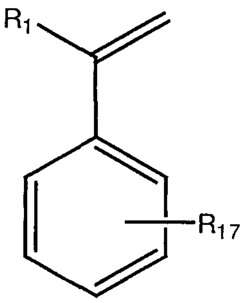
28. The silicone hydrogel of claim 26 wherein said silicone-containing component comprises at least one hydroxyl group.

29. The silicone hydrogel of claim 26 further comprising at least one hydroxyalkyl monomer.

30. The silicone hydrogel of claim 29 wherein said hydroxyalkyl monomer is selected from hydroxyalkyl (meth)acrylate or (meth)acrylamide monomer of Formula VII or a styryl compound of Formula VIII



FORMULA VII



FORMULA VIII

wherein R_1 is H or methyl,
X is O or NR_{16}, R_{16} is a H, C_1 to C_4 alkyl, which may be further substituted with at least one OH, and
R_{17} is selected from C_2-C_4 mono or dihydroxy substituted alkyl, and poly(ethylene glycol) having 1-10 repeating units.

31. The silicone hydrogel of claim 30 wherein:

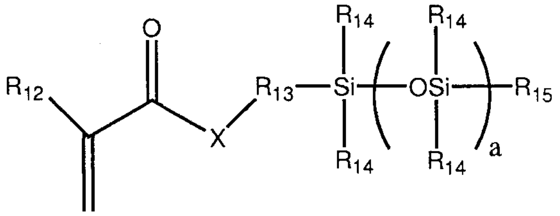
i) R_1 is H or methyl, X is oxygen and R is selected from C_2-C_4 mono or dihydroxy substituted alkyl, and poly(ethylene glycol) having 1-10 repeating units; or
ii) R_1 is methyl, X is oxygen and R_{17} is selected from C_2-C_4 mono or dihydroxy substituted alkyl, and poly(ethylene glycol) having 2-20 repeating units.

32. The silicone hydrogel of claim 29

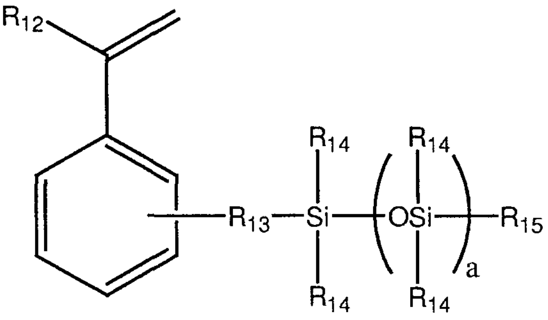
i) wherein said hydroxyalkyl monomer is selected from 2-hydroxyethyl methacrylate, 2-hydroxyethyl acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 1-hydroxypropyl-2-(meth)acrylate, 2-hydroxy-2-methylpropyl (meth)acrylate, 3-hydroxy-2,2-dimethyl-propyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, glycerol (meth)acrylate, 2-hydroxyethyl (meth)acrylamide, polyethyleneglycol monomethacrylate, bis-(2-hydroxyethyl) (meth)acrylamide, 2,3-dihydroxypropyl (meth)acrylamide, and mixtures thereof; or
ii) wherein said hydroxyalkyl monomer is selected from the group consisting of 2-hydroxyethyl methacrylate, glycerol methacrylate, 2-hydroxypropyl methacrylate, hydroxybutyl methacrylate, 3-hydroxy-2,2-dimethyl-propyl methacrylate, and mixtures thereof; or
iii) wherein said hydroxyalkyl monomer comprises 2-hydroxyethyl methacrylate, 3-hydroxy-2,2-dimethyl-propyl methacrylate, glycerol methacrylate and mixtures comprising them.

33. The silicone hydrogel of claim 1 wherein the at least one silicone-containing monomer is monofunctional and comprises (a) a reactive group selected from (meth)acrylates, styryls, amides and mixtures thereof and (b) a polydialkyl siloxane chain and may optionally contain fluorine.

34. The silicone hydrogel of claim 1 wherein said silicone-containing component is selected from mono (meth)acryloxyalkyl polydialkylsiloxane monomer of Formula IX or the styryl polydialkylsiloxane monomer of Formula X:



Formula IX



Formula X

wherein R_{12} is H or methyl;
X is O or NR_{16};
each R_{14} is independently a C_1 to C_4 alkyl which may be fluorine substituted, or phenyl;
R_{15} is a C_1 to C_4 alkyl;
R_{13} is a divalent alkyl group, which may further be functionalized with a group selected from the group consisting of ether groups, hydroxyl groups, carbamate groups and combinations thereof;
a is 3 to 50;
R_{16} is selected from H, C_{1-4}, which may be further substituted with one or more hydroxyl groups.

35. The silicone hydrogel of claim 34 wherein:

i) each R_{14} is independently selected from ethyl and methyl groups; or
ii) all R_{14} are methyl.

36. The silicone hydrogel of claim 34

i) wherein R_{12} and each R_{14} are methyl; or
ii) wherein at least one R_{14} is 3,3,3-trifluoropropyl; or
iii) wherein R_{13} is selected from C_1-C_6 alkylene groups which may be substituted with ether, hydroxyl and combinations thereof; or
iv) wherein R_{13} is selected from C_1 or C_3-C_6 alkylene groups which may be substituted with ether, hydroxyl and combinations thereof; or
v) wherein a is 5 to 15; or
vi) wherein R_{16} is H or methyl; or
vii) wherein said monomethacryloxyalkylpolydimethylsiloxane methacrylate is selected from the group consisting of monomethacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane, monomethacryloxypropyl terminated mono-n-methyl terminated polydimethylsiloxane, monomethacryloxypropyl terminated mono-n-butyl terminated polydiethylsiloxane, monomethacryloxypropyl terminated mono-n-methyl terminated polydiethylsiloxane, N-(2,3-dihydroxypropane)-N'-(propyl tetra(dimethylsiloxy) dimethylbutylsilane)acrylamide, α-(2-hydroxy-1-methacryloxypropyloxypropyl)-ω-butyl-octamethylpentasiloxane, and mixtures thereof; or
viii) wherein said monomethacryloxyalkylpolydimethylsiloxane methacrylate is selected from the group consisting of monomethacryloxypropyl terminated mono-n-butyl terminated polydimethylsiloxane, monomethacryloxypropyl terminated mono-n-methyl terminated polydimethylsiloxane, N-(2,3-dihydroxypropane)-N'-(propyl tetra(dimethylsiloxy) dimethylbutylsilane)acrylamide, and mixtures thereof.

37. The silicone hydrogel of any preceding claim further comprising

i) at least one crosslinking monomer; and/or
ii) further comprising at least one photoinitiator.

38. The silicone hydrogel of any preceding claim further comprising an advancing contact angle of:

i) less than 80°; or
ii) less than 70°.

39. The silicone hydrogel of any preceding claim further comprising from 5 to 20 wt% of at least one polar diluent, based upon all components in the reaction mixture.

40. The silicone hydrogel of any preceding claim wherein said reaction mixture comprises less than 5% of intermediate reacting hydrophilic components.

41. The silicone hydrogel of any preceding claim dependent on claim 8 wherein said at least one slow reacting crosslinker and at least one fast reacting crosslinker are each present in said reaction mixture in amounts between:

i) 0.05 to 0.3 wt%; or
ii) 0.1 to 0.2 wt%.

42. The silicone hydrogel of any preceding claim dependent on claim 8 wherein all crosslinkers are present in an amount between 0.5 wt% and 2 wt%.

Patentansprüche

1. Silikonhydrogel, gebildet aus einer Reaktionsmischung, umfassend:

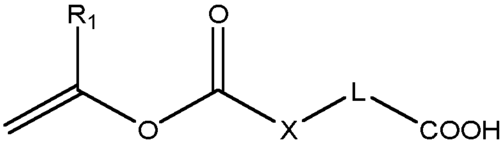
30 bis 75 Gew.-% einer Mischung langsam reagierender hydrophiler Monomere, jeweils mit einer kinetischen Halbwertszeit eines langsam reagierenden hydrophilen Monomers, wobei die Mischung langsam reagierender hydrophiler Monomere mindestens ein langsam reagierendes anionisches Monomer mit mindestens einer aus Carbonsäuren, Sulfonsäuren und deren Salzen und Mischungen davon ausgewählten anionischen Gruppe umfasst;
mindestens eine silikonhaltige Komponente mit einer kinetischen Halbwertszeit einer silikonhaltigen Komponente, die gegebenenfalls durch mindestens eine hydroxylgruppenhaltige Gruppe substituiert sein kann; und
mindestens eine hydroxylgruppenhaltige Komponente, die aus der durch mindestens eine hydroxylgruppenhaltige Gruppe substituierten silikonhaltigen Komponente, mindestens einem Hydroxyalkylmonomer und Mischungen davon ausgewählt ist,
wobei das Verhältnis der Halbwertszeiten der langsam reagierenden hydrophilen Komponenten zur Halbwertszeit der silikonhaltigen Komponente jeweils mindestens 2 beträgt.

2. Silikonhydrogel nach Anspruch 1, wobei die Reaktionsmischung

37 bis 75 Gew.-% oder
37 bis 70 Gew.-% oder
39 bis 60 Gew.-% mindestens eines langsam reagierenden hydrophilen Monomers mit einer kinetischen Halbwertszeit eines langsam reagierenden hydrophilen Monomers umfasst.

3. Silikonhydrogel nach einem der vorhergehenden Ansprüche,
wobei die langsam reagierende anionische Komponente reaktive Funktionalität aus der Gruppe bestehend aus reaktiven Methacrylamidgruppen, N-Vinylamiden, O-Vinylcarbamaten, O-Vinylcarbonaten, N-Vinylcarbamaten, O-Vinylethern und O-2-Propenyl umfasst, wobei die Vinyl- bzw. Allylgruppen weiter durch eine Methylgruppe substituiert sein können.

4. Silikonhydrogel nach einem der vorhergehenden Ansprüche, wobei die langsam reagierende anionische Komponente aus der Gruppe bestehend aus 4-Acrylamidobutansäure (ACAII), 3-Acrylamidopropionsäure, 5-Acrylamidopentansäure, 3-Acrylamido-3-methylbutansäure (AMBA), N-Vinyloxycarbonyl-α-alanin, N-Vinyloxycarbonyl-β-alanin (VINAL), Vinylsulfonatsalz, (2-Carboxymethoxy)essigsäure-1-ethenylester der Formel



Formel Q,

wobei R_1 für H oder Methyl steht, X für O oder NR_{16} steht, R_{16} für H oder C_{1-3}-Alkyl steht und L für eine zweiwertige C_{1-4}-Alkylgruppe steht, und Mischungen davon ausgewählt ist, gegebenenfalls
wobei die langsam reagierende anionische Komponente aus der Gruppe bestehend aus N-Vinyloxycarbonyl-α-alanin, N-Vinyloxycarbonyl-β-alanin (VINAL), Vinylsulfonat-Natriumsalz, (2-Carboxymethoxy)essigsäure-1-ethenylester der Formel Q, Mischungen davon und dergleichen ausgewählt ist.

5. Silikonhydrogel nach einem der Ansprüche 1-3, wobei die langsam reagierende anionische Komponente in der reaktiven Mischung in einer Menge von weniger als 20 Mol-% vorliegt.

6. Silikonhydrogel nach einem der Ansprüche 1-3, wobei die langsam reagierende anionische Komponente in der reaktiven Mischung in einer Menge zwischen

i) 0,5 und 15 Mol-% oder
ii) 0,5 und 5 Mol-% oder
iii) 0,5 und 10 Mol-%,

bezogen auf alle Komponenten in der Reaktionsmischung, vorliegt.

7. Silikonhydrogel nach einem der vorhergehenden Ansprüche, wobei alle langsam reagierenden Komponenten die gleiche reaktive Funktionalität aufweisen, gegebenenfalls wobei alle langsam reagierenden Komponenten Vinylfunktionalität aufweisen.

8. Silikonhydrogel nach einem der vorhergehenden Ansprüche, wobei die Reaktionsmischung ferner mindestens einen langsam reagierenden Vernetzer und mindestens einen schnell reagierenden Vernetzer umfasst.

9. Silikonhydrogel nach Anspruch 8, wobei die langsam reagierenden Vernetzer nur reaktive Vinylfunktionalität aufweisen und die schnell reagierenden Vernetzer nur reaktive (Meth)acrylatfunktionalität aufweisen, gegebenenfalls wobei der langsam reagierende Vernetzer Triallylcyanurat (TAC) umfasst und der schnell reagierende Vernetzer aus der Gruppe bestehend aus Ethylenglykoldimethylacrylat (EGDMA), Tetraethylenglykoldimethacrylat (TEGDMA) und Mischungen davon ausgewählt ist.

10. Silikonhydrogel nach Anspruch 7 oder 8, wobei der mindestens eine langsam reagierende Vernetzer und der mindestens eine schnell reagierende Vernetzer in der Reaktionsmischung jeweils in Mengen zwischen

i) 0,4 bis 2,0 mmol pro 100 g reaktive Komponenten oder
ii) 0,3 bis etwa 2,0 mmol/100 g polymerisierbarer Komponenten

vorliegen.

11. Silikonhydrogel nach einem der vorhergehenden Ansprüche, wobei die reaktive Mischung ferner mindestens eine reaktive kationische Komponente umfasst, gegebenenfalls
wobei die kationische Komponente bzw. wasserstoffbindende Komponente in einer zur Verbesserung der Oberflächenelastizität des Hydrogels ausreichenden Menge vorliegt.

12. Silikonhydrogel nach Anspruch 11, wobei die mindestens eine reaktive kationische Komponente die gleiche reaktive Funktionalität wie mindestens eine der silikonhaltigen Komponenten aufweist.

13. Silikonhydrogel nach einem der vorhergehenden Ansprüche, wobei das Verhältnis der kinetischen Halbwertszeiten mindestens 3 beträgt.

14. Silikonhydrogel nach einem der vorhergehenden Ansprüche, das ferner einen Dk-Wert von

i) mindestens 80 Barrer oder
ii) mindestens 85 Barrer aufweist, wobei der Dk-Wert gemäß der im Abschnitt "Sauerstoffdurchlässigkeit (Dk)" der näheren Beschreibung beschriebenen Methode gemessen wird.

15. Silikonhydrogel nach einem der vorhergehenden Ansprüche, das ferner eine prozentuale Trübung von

i) weniger als 70 % oder
ii) weniger als 50 % aufweist, wobei die prozentuale Trübung gemäß der im Abschnitt "Trübungsmessung" der "Trübungslöslichkeitsparameter" der näheren Beschreibung beschriebenen Methode gemessen wird.

16. Silikonhydrogel nach einem der vorhergehenden Ansprüche, das ferner einen Wassergehalt von

i) mindestens 55 % oder
ii) mindestens 60 % aufweist.

17. Silikonhydrogel nach einem der vorhergehenden Ansprüche, das ferner einen Modul von

i) weniger als 150 psi oder
ii) 100 psi oder weniger aufweist, wobei der Modul gemäß der im Abschnitt "Modul" der näheren Beschreibung beschriebenen Methode gemessen wird.

18. Silikonhydrogel nach einem der vorhergehenden Ansprüche, wobei die Reaktionsmischung ferner mindestens eine UV-absorbierende Verbindung umfasst.

19. Silikonhydrogel nach Anspruch 18, wobei die mindestens eine UV-absorbierende Verbindung reaktiv ist.

20. Silikonhydrogel nach Anspruch 19, wobei die mindestens eine UV-absorbierende Verbindung aus

i) Benzotriazolen oder
ii) der Gruppe bestehend aus reaktiven 2-(2'-Hydroxyphenyl)benzotriazolen, 2-Hydroxybenzophenonen, 2-Hydroxyphenyltriazinen, Oxaniliden, Cyanoacrylaten, Salicylaten und 4-Hydroxybenzoaten oder
iii) der Gruppe bestehend aus 2-(2'-Hydroxy-5-methacrylyloxyethylphenyl)-2H-benzotriazol, 5-Vinyl- und 5-Isopropenylderivaten von 2-(2,4-Dihydroxyphenyl)-2H-benzotriazol und 4-Acrylaten oder 4-Methacrylaten von 2-(2,4-Dihydroxyphenyl)-2H-benzotriazol oder 2-(2,4-Dihydroxyphenyl)-1,3-2H-dibenzotriazol und Mischungen davon ausgewählt ist.

21. Silikonhydrogel nach Anspruch 19, umfassend zwischen

i) 0,5 und 4 Gew.-% mindestens eines UV-Absorbers oder
ii) 1 Gew.-% und 2 Gew.-% UV-Absorber.

22. Silikonhydrogel nach einem der vorhergehenden Ansprüche, wobei die Reaktionsmischung frei von Verdünnungsmittel ist und/oder
wobei die Reaktionsmischung frei von 3-Methacryloxypropyltris(trimethylsiloxy)silan (TRIS) ist.

23. Silikonhydrogel nach einem der vorhergehenden Ansprüche, wobei i) das langsam reagierende hydrophile Monomer eine reaktive Gruppe aus der Gruppe bestehend aus (Meth)acrylamiden, Vinylgruppen, Allylgruppen und Kombinationen davon umfasst und die silikonhaltige Komponente eine reaktive Gruppe aus der Gruppe bestehend aus (Meth)acrylaten, Styrylen, Amiden und Mischungen davon umfasst und/oder
ii) das langsam reagierende hydrophile Monomer eine reaktive Gruppe aus der Gruppe bestehend aus Vinylgruppen, Allylgruppen und Kombinationen davon umfasst und die silikonhaltige Komponente eine reaktive Gruppe aus der Gruppe bestehend aus (Meth)acrylaten, Styrylen, Amiden und Mischungen davon umfasst.

24. Silikonhydrogel nach einem der vorhergehenden Ansprüche, wobei das langsam reagierende hydrophile Monomer in einer Menge zwischen

i) 39 und 70 Gew.-% oder
ii) 39 und 60 Gew.-%

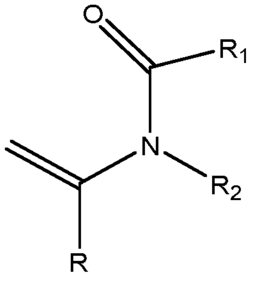
vorliegt.

25. Silikonhydrogel nach einem der vorhergehenden Ansprüche,

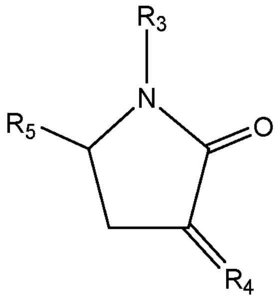
i) wobei das langsam reagierende hydrophile Monomer eine reaktive Gruppe aus der Gruppe bestehend aus

N-Vinylamiden, O-Vinylcarbamaten, O~ Vinylcarbonaten, N-Vinylcarbamaten, O-Vinylethern und O-2-Propenyl, wobei die Vinyl- bzw. Allylgruppen weiter durch eine Methylgruppe substituiert sein können, umfasst und/oder
ii) wobei das langsam reagierende hydrophile Monomer mindestens eine hydrophile Gruppe aus der Gruppe bestehend aus Hydroxylgruppen, Aminen, Ethern, Amiden, Ammoniumgruppen, Carbonsäure, Carbamaten und Kombinationen davon umfasst und/oder
iii) wobei das langsam reagierende hydrophile Monomer mindestens eine hydrophile Gruppe aus der Gruppe bestehend aus Hydroxylgruppen, Ethern, Amiden, Carbonsäure und Kombinationen davon umfasst.

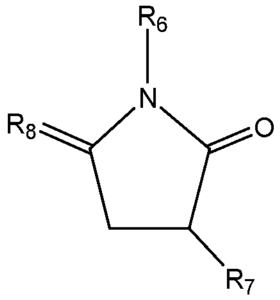
26. Silikonhydrogel nach Anspruch 1, wobei das langsam reagierende hydrophile Monomer aus N-Vinylamid-Monomer der Formel I, einem Vinylpyrrolidon der Formel II-IV, N-Vinylpiperidon der Formel V:



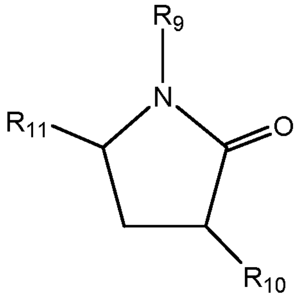
Formel I



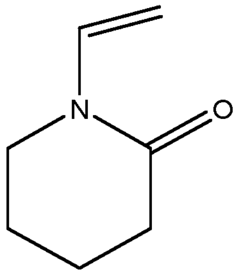
Formel II



Formel III



Formel IV



Formel V

ausgewählt ist,

wobei R für H oder Methyl steht;
R_1, R_2, R_3, R_6, R_7, R_{10} und R_{11} unabhängig voneinander aus H, CH_3, CH_2CH_3, $CH_2CH_2CH_3$ und $C(CH_3)_2$ ausgewählt sind;
R_4 und R_8 unabhängig voneinander aus CH_2, $CHCH_3$ und $C(CH_3)$ ausgewählt sind;
R_5 aus H, Methyl und Ethyl ausgewählt ist und
R_9 aus $CH{=}CH_2$, $CCH_3{=}CH_2$ und $CH{=}CHCH_3$ ausgewählt ist.

27. Silikonhydrogel nach Anspruch 26, wobei:

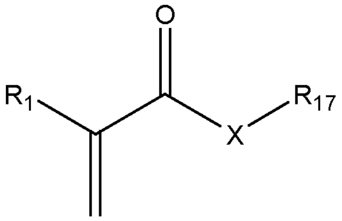
i) das langsam reagierende hydrophile Monomer aus dem Vinylpyrrolidon der Formel II oder IV oder dem N-Vinylamid-Monomer der Formel I ausgewählt ist und die Gesamtzahl von Kohlenstoffatomen in R_1 und R_2 4 oder weniger beträgt oder

ii) das langsam reagierende hydrophile Monomer aus einem Vinylpyrrolidon der Formel III oder IV ausgewählt ist und R_6 für Methyl steht, R_7 für Wasserstoff steht, Rg für CH=CH_2 steht, R_{10} und R_{11} für H stehen, oder
iii) das langsam reagierende hydrophile Monomer aus Ethylenglykolvinylether (EGVE), Di(ethylenglykol)vinylether (DEGVE), N-Vinylpyrrolidon (NVP), 1-Methyl-3-methylen-2-pyrrolidon, 1-Methyl-5-methylen-2-pyrrolidon, 5-Methyl-3-methylen-2-pyrrolidon, 1-Ethyl-5-methylen-2-pyrrolidon, N-Methyl-3-methylen-2-pyrrolidon, 5-Ethyl-3-methylen-2-pyrrolidon, 1-n-Propyl-3-methylen-2-pyrrolidon, 1-n-Propyl-5-methylen-2-pyrrolidon, 1-Isopropyl-3-methylen-2-pyrrolidon, 1-Isopropyl-5-methylen-2-pyrrolidon, N-Vinyl-N-methylacetamid (VMA), N-Vinyl-N-ethylacetamid, N-Vinyl-N-ethylformamid, N-Vinylformamid, N-Vinylacetamid, N-Vinylisopropylamid, Allylalkohol, N-Vinylcaprolactam, N-2-Hydroxyethylvinylcarbamat, N-Carboxy-β-alanin-N-vinylester, N-Carboxyvinyl-β-alanin (VINAL), N-Carboxyvinyl-α-alanin und Mischungen davon ausgewählt ist oder
iii) wobei das langsam reagierende hydrophile Monomer aus NVP, VMA und 1-Methyl-5-methylen-2-pyrrolidon ausgewählt ist oder
iv) wobei das langsam reagierende hydrophile Monomer NVP umfasst.

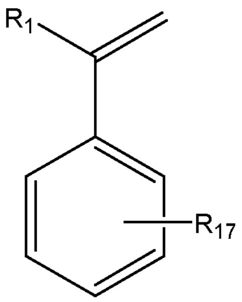
28. Silikonhydrogel nach Anspruch 26, wobei die silikonhaltige Komponente mindestens eine Hydroxylgruppe umfasst.

29. Silikonhydrogel nach Anspruch 26, das ferner mindestens ein Hydroxyalkylmonomer umfasst.

30. Silikonhydrogel nach Anspruch 29, wobei das Hydroxyalkylmonomer aus Hydroxyalkyl(meth)acrylat- oder (Meth)acrylamid-Monomer der Formel VII oder einer Styrylverbindung der Formel VIII



FORMEL VII



FORMEL VIII

ausgewählt ist,

wobei R_1 für H oder Methyl steht,
X für O oder NR_{16} steht, R_{16} für H oder C_1- bis C_4-Alkyl, das gegebenenfalls durch mindestens ein OH substituiert sein kann, steht und
R_{17} aus mono- oder dihydroxysubstituiertem C_2-C_4-Alkyl und Poly(ethylenglykol) mit 1-10 Wiederholungseinheiten ausgewählt ist.

31. Silikonhydrogel nach Anspruch 30, wobei

i) R_1 für H oder Methyl steht, X für Sauerstoff steht und R aus mono- oder dihydroxysubstituiertem C_2-C_4-Alkyl und Poly(ethylenglykol) mit 1-10 Wiederholungseinheiten ausgewählt ist oder
ii) R_1 für Methyl steht, X für Sauerstoff steht und R_{17} aus mono- oder dihydroxysubstituiertem C_2-C_4-Alkyl und Poly(ethylenglykol) mit 2-20 Wiederholungseinheiten ausgewählt ist.

32. Silikonhydrogel nach Anspruch 29,

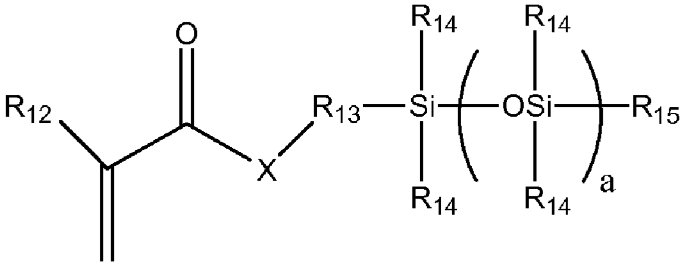
i) wobei das Hydroxyalkylmonomer aus 2-Hydroxyethylmethacrylat, 2-Hydroxyethylacrylat, 3-Hydroxypropyl(meth)acrylat, 2-Hydroxypropyl(meth)-acrylat, 1-Hydroxypropyl-2-(meth)acrylat, 2-Hydroxy-2-methylpropyl(meth)acrylat, 3-Hydroxy-2,2-dimethylpropyl(meth)acrylat, 4-Hydroxybutyl-(meth)acrylat, Glycerin(meth)acrylat, 2-Hydroxyethyl(meth)acrylamid, Polyethylenglykolmonomethacrylat, Bis-(2-hydroxyethyl)(meth)acrylamid, 2,3-Dihydroxypropyl(meth)acrylamid und Mischungen davon ausgewählt ist oder
ii) wobei das Hydroxyalkylmonomer aus der Gruppe bestehend aus 2-Hydroxyethylmethacrylat, Glycerinmethacrylat, 2-Hydroxypropylmethacrylat, Hydroxybutylmethacrylat, 3-Hydroxy-2,2-dimethylpropylmethacrylat

und Mischungen davon bestehenden Gruppe ausgewählt ist oder

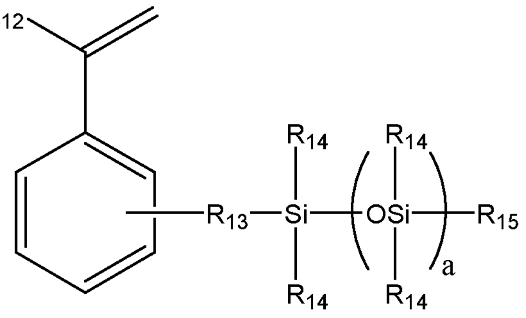
iii) wobei das Hydroxyalkylmonomer 2-Hydroxyethylmethacrylat, 3-Hydroxy-2,2-dimethylpropylmethacrylat, Glycerinmethacrylat und diese umfassende Mischungen umfasst.

33. Silikonhydrogel nach Anspruch 1, wobei das mindestens eine silikonhaltige Monomer monofunktionell ist und (a) eine aus (Meth)acrylaten, Styrylen, Amiden und Mischungen davon ausgewählte reaktive Gruppe und (b) eine Polydialkylsiloxankette umfasst und gegebenenfalls Fluor enthalten kann.

34. Silikonhydrogel nach Anspruch 1, wobei die silikonhaltige Komponente aus dem Mono(meth)acryloxyalkylpolydialkylsiloxanmonomer der Formel IX oder dem Styrolpolydialkylsiloxanmonomer der Formel X ausgewählt ist:



Formel IX



Formel X,

wobei R_{12} für H oder Methyl steht;
X für O oder NR_{16} steht;
R_{14} jeweils unabhängig für ein C_1- bis C_4-Alkyl, das fluorsubstituiert sein kann, oder Phenyl steht;
R_{15} für C_1- bis C_4-Alkyl steht;
R_{13} für eine zweiwertige Alkylgruppe steht, die weiter durch eine aus der Gruppe bestehend aus Ethergruppen, Hydroxylgruppen, Carbamatgruppen und Kombinationen davon ausgewählte Gruppe funktionalisiert sein kann;
a für 3 bis 50 steht;
R_{16} aus H und C_{1-4}, das weiter durch eine oder mehrere Hydroxylgruppen substituiert sein kann, ausgewählt ist.

35. Silikonhydrogel nach Anspruch 34, wobei:

i) R_{14} jeweils unabhängig aus Ethyl- und Methylgruppen ausgewählt ist oder
ii) alle R_{14} für Methyl stehen.

36. Silikonhydrogel nach Anspruch 34,

i) wobei R_{12} und jedes R_{14} für Methyl stehen oder
ii) wobei mindestens ein R_{14} für 3,3,3-Trifluorpropyl steht oder
iii) wobei R_{13} aus C_1-C_6-Alkylengruppen, die durch Ether, Hydroxyl und Kombinationen davon substituiert sein können, ausgewählt ist oder
iv) wobei R_{13} aus C_1- oder C_3-C_6-Alkylengruppen, die durch Ether, Hydroxyl und Kombinationen davon substituiert sein können, ausgewählt ist oder
v) wobei a für 5 bis 15 steht oder

vi) wobei R_{16} für H oder Methyl steht oder
vii) wobei das Monomethacryloxyalkylpolydimethylsiloxanmethacrylat aus der Gruppe bestehend aus monomethacryloxypropylterminiertem mono-n-butylterminiertem Polydimethylsiloxan, monomethacryloxypropylterminiertem mono-n-methylterminiertem Polydimethylsiloxan, monomethacryloxypropylterminiertem mono-n-butylterminiertem Polydiethylsiloxan, monomethacryloxypropylterminiertem mono-n-methylterminiertem Polydiethylsiloxan, N-(2,3-Dihydroxypropan)-N'-(propyltetra(dimethylsiloxy)dimethylbutylsilan)acrylamid, α-(2-Hydroxy-1-methacryloxypropyloxypropyl)-ω-butyloctamethylpentasiloxan und Mischungen davon ausgewählt ist oder
viii) wobei das Monomethacryloxyalkylpolydimethylsiloxanmethacrylat aus der Gruppe bestehend aus monomethacryloxypropylterminiertem mono-n-butylterminiertem Polydimethylsiloxan, monomethacryloxypropylterminiertem mono-n-methylterminiertem Polydimethylsiloxan, N-(2,3-Dihydroxypropan)-N'-(propyltetra(dimethylsiloxy)dimethylbutylsilan)-acrylamid und Mischungen davon ausgewählt ist.

37. Silikonhydrogel nach einem der vorhergehenden Ansprüche, ferner umfassend

i) mindestens ein vernetzendes Monomer und/oder
ii) ferner umfassend mindestens einen Photoinitiator.

38. Silikonhydrogel nach einem der vorhergehenden Ansprüche, das ferner einen Fortschreitkontaktwinkel von:

i) weniger als 80° oder
ii) weniger als 70°

aufweist.

39. Silikonhydrogel nach einem der vorhergehenden Ansprüche, ferner umfassend 5 bis 20 Gew.-% mindestens eines polaren Verdünnungsmittels, bezogen auf alle Komponenten in der Reaktionsmischung.

40. Silikonhydrogel nach einem der vorhergehenden Ansprüche, wobei die Reaktionsmischung weniger als 5 % mittelschnell reagierende hydrophile Komponenten umfasst.

41. Silikonhydrogel nach einem der vorhergehenden Ansprüche, abhängig von Anspruch 8, wobei der mindestens eine langsam reagierende Vernetzer und der mindestens eine schnell reagierende Vernetzer in der Reaktionsmischung jeweils in Mengen zwischen

i) 0,05 bis 0,3 Gew.-% oder
ii) 0,1 bis 0,2 Gew.-%

vorliegen.

42. Silikonhydrogel nach einem der vorhergehenden Ansprüche, abhängig von Anspruch 8, wobei alle Vernetzer in einer Menge zwischen 0,5 Gew.-% und 2 Gew.-% vorliegen.

Revendications

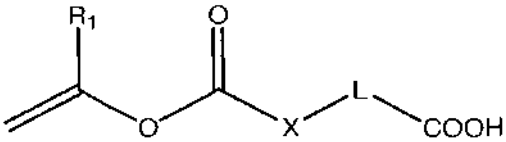
1. Hydrogel de silicone formé d'un mélange de réaction comprenant :

30 à 75 % en poids d'un mélange de monomères hydrophiles à réaction lente, ayant chacun une demi-vie cinétique de monomère hydrophile à réaction lente, ledit mélange de monomères hydrophiles à réaction lente comprenant au moins un monomère anionique à réaction lente comprenant au moins un groupe anionique choisi parmi des acides carboxyliques, des acides sulfoniques et leurs sels et des mélanges de ceux-ci ;
au moins un composant contenant une silicone ayant une demi-vie cinétique de composant contenant une silicone, qui peut être facultativement substitué par au moins un groupe contenant hydroxyle ; et
au moins un composant contenant hydroxyle choisi parmi ledit composant contenant une silicone substitué par au moins un groupe contenant hydroxyle, au moins un monomère d'hydroxyalkyle, et des mélanges de ceux-ci, dans lequel le rapport de chacune desdites demi-vies de composant hydrophile à réaction lente à ladite demi-vie de composant contenant une silicone est au moins 2.

2. Hydrogel de silicone selon la revendication 1 dans lequel le mélange de réaction comprend ;
37 à 75 % en poids ; ou
37 à 70 % en poids ; ou
39 à 60 % en poids, d'au moins un monomère hydrophile à réaction lente ayant une demi-vie cinétique de monomère hydrophile à réaction lente.

3. Hydrogel de silicone selon l'une quelconque des revendications précédentes
dans lequel ledit composant anionique à réaction lente comprend une fonctionnalité réactive choisie dans le groupe constitué de groupes réactifs méthacrylamide, N-vinylamides, carbamates de O-vinyle, carbonates de O-vinyle, carbamates de N-vinyle, éthers O-vinyliques, O-2-propényle, dans lequel les groupes vinyle ou allyle peuvent en outre être substitués par un groupe méthyle.

4. Hydrogel de silicone selon l'une quelconque des revendications précédentes dans lequel ledit composant anionique à réaction lente est choisi parmi, le groupe constitué de l'acide 4-acrylamidobutanoïque (ACAII), l'acide 3-acrylamidopropionique, l'acide 5-acrylamidopentanoïque, l'acide 3-acrylamido-3-méthylbutanoïque (AMBA), la N-vinyloxycarbonyl-α-alanine, la N-vinyloxycarbonyl-β-alanine (VINAL), sel de vinylsulfonate ; l'ester 2-carboxyméthoxy)-1-éthénylique d'acide acétique, de formule



Formule Q

où R_1 est H ou méthyle, X est O ou NR_{16}, R_{16} est H ou alkyle en C_{1-3}, et L est un groupe alkyle en C_{1-4} divalent ; et des mélanges de ceux-ci, facultativement
dans lequel ledit composant anionique à réaction lente est choisi dans le groupe constitué de la N-vinyloxycarbonyl-α-alanine ; la N-vinyloxycarbonyl-β-alanine (VINAL) ; le sel de sodium de vinylsulfonate ; l'acide acétique, des esters 2-carboxyméthoxy)-1-éthényliques d'acide acétique de formule Q, des mélanges de ceux-ci et similaire.

5. Hydrogel de silicone selon l'une quelconque des revendications 1 à 3 dans lequel ledit composant anionique à réaction lente est présent dans le mélange de réactifs en une quantité inférieure à 20 % en moles.

6. Hydrogel de silicone selon l'une quelconque des revendications 1 à 3 dans lequel ledit composant anionique à réaction lente est présent dans le mélange de réactifs en une quantité comprise entre :

i) 0,5 et 15 % en moles ; ou
ii) 0,5 et 5 % en moles ; ou
iii) 0,5 et 10 % en moles,

sur la base de la totalité des composants dans le mélange de réaction.

7. Hydrogel de silicone selon l'une quelconque des revendications précédentes dans lequel tous lesdits composants à réaction lente ont la même fonctionnalité réactive, facultativement dans lequel tous lesdits composants à réaction lente ont une fonctionnalité vinyle.

8. Hydrogel de silicone selon l'une quelconque des revendications précédentes dans lequel ledit mélange de réaction comprend en outre au moins un agent de réticulation à réaction lente et au moins un agent de réticulation à réaction rapide.

9. Hydrogel de silicone selon la revendication 8 dans lequel lesdits agents de réticulation à réaction lente ont uniquement une fonctionnalité vinyle réactive et lesdits agents de réticulation à réaction rapide ont une fonctionnalité réactive (méth)acrylate uniquement, facultativement
dans lequel ledit agent de réticulation à réaction lente comprend le cyanurate de triallyle (TAC) et ledit agent de réticulation à réaction rapide est choisi dans le groupe constitué du diméthylacrylate d'éthylène glycol (EGDMA), du diméthacrylate de tétraéthylèneglycol (TEGDMA) et des mélanges de ceux-ci.

10. Hydrogel de silicone selon les revendications 7 ou 8, dans lequel ledit au moins un agent de réticulation à réaction lente et au moins un agent de réticulation à réaction rapide sont chacun présents dans ledit mélange de réaction dans des quantités comprises entre :

i) 0,4 et 2,0 mmoles par 100 g de composants réactifs ; ou
ii) 0,3 à environ 2,0 mmol/100 g de composants polymérisables.

11. Hydrogel de silicone selon l'une quelconque des revendications précédentes dans lequel ledit mélange de réactifs comprend en outre au moins un composant cationique réactif, facultativement
dans lequel ledit composant cationique ou le composant de liaison hydrogène est présent en une quantité suffisante pour améliorer l'élasticité de surface dudit hydrogel.

12. Hydrogel de silicone selon la revendication 11 dans lequel ledit au moins un composant cationique réactif a la même fonctionnalité réactive qu'au moins un desdits composants contenant une silicone.

13. Hydrogel de silicone selon l'une quelconque des revendications précédentes dans lequel ledit rapport de demi-vie cinétique est au moins 3.

14. Hydrogel de silicone selon l'une quelconque des revendications précédentes comprenant en outre un Dk de :

i) au moins 80 barrers ; ou
ii) au moins 85 barrers, dans lequel Dk est mesuré selon le procédé décrit dans la section « Perméabilité d'oxygène (Dk) » de la description détaillée.

15. Hydrogel de silicone selon l'une quelconque des revendications précédentes comprenant en outre un % trouble de :

i) moins de 70 % ; ou
ii) moins de 50 %, dans lequel le % trouble est mesuré selon le procédé décrit dans la section « Mesure du trouble » du « Paramètre de solubilité de trouble » de la description détaillée.

16. Hydrogel de silicone selon l'une quelconque des revendications précédentes comprenant en outre une teneur en eau de :

i) au moins 55 % ; ou
ii) au moins 60 %.

17. Hydrogel de silicone selon l'une quelconque des revendications précédentes comprenant en outre un module de :

i) moins de 150 psi ; ou
ii) 100 psi ou moins, dans lequel le module est mesuré selon le procédé décrit dans la section « Module » de la description détaillée.

18. Hydrogel de silicone selon l'une quelconque des revendications précédentes dans lequel ledit mélange de réaction comprend en outre au moins un composé absorbant les UV.

19. Hydrogel de silicone selon la revendication 18 dans lequel ledit au moins un composé absorbant les UV est réactif.

20. Hydrogel de silicone selon la revendication 19 dans lequel ledit au moins un composé absorbant les UV est choisi parmi :

i) des benzotriazoles ; ou
ii) le groupe constitué des 2-(2'-hydroxyphényl)benzotriazoles, 2-hydroxybenzophénones, 2-hydroxyphényltriazines, oxanilides, cyanoacrylates, salicylates et 4-hydroxybenzoates réactifs ; ou
iii) le groupe constitué de 2-(2'-hydroxy-5-méthacrylyloxyéthylphényl)-2H-benzotriazole, dérivés 5-vinyle et 5-isopropényle de 2-(2,4-dihydroxyphényl)-2H-benzotriazole et 4-acrylates ou 4-méthacrylates de 2-(2,4-dihydroxyphényl)-2H-benzotriazole ou 2-(2,4-dihydroxyphényl)-1,3-2H-dibenzotriazole, et des mélanges de ceux-ci.

21. Hydrogel de silicone selon la revendication 19 comprenant entre :

i) 0,5 et 4 % en poids d'au moins un absorbeur UV ; ou
ii) 1 % en poids et 2 % en poids d'absorbeur UV.

22. Hydrogel de silicone selon l'une quelconque des revendications précédentes dans lequel ledit mélange de réaction est exempt de diluant, et/ou
dans lequel ledit mélange de réaction est exempt de 3-méthacryloxypropyltris(triméthylsiloxy)silane (TRIS).

23. Hydrogel de silicone selon l'une quelconque des revendications précédentes dans lequel i) ledit monomère hydrophile à réaction lente comprend un groupe réactif choisi dans le groupe constitué de (méth)acrylamides, vinyles, allyles et des combinaisons de ceux-ci et ledit composant contenant une silicone comprend un groupe réactif choisi dans le groupe constitué de (méth)acrylates, styryles, amides et des mélanges de ceux-ci, et/ou
ii) ledit monomère hydrophile à réaction lente comprend un groupe réactif choisi dans le groupe constitué de vinyles, allyles et des combinaisons de ceux-ci et ledit composant contenant une silicone comprend un groupe réactif choisi dans le groupe constitué des (méth)acrylates, styryles, amides et des mélanges de ceux-ci.

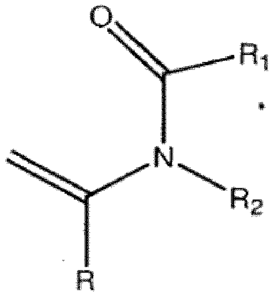
24. Hydrogel de silicone selon l'une quelconque des revendications précédentes dans lequel ledit monomère hydrophile à réaction lente est présent en une quantité comprise entre :

i) 39 et 70 % en poids ; ou
ii) 39 et 60 % en poids.

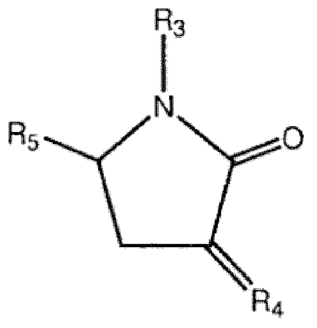
25. Hydrogel de silicone selon l'une quelconque des revendications précédentes

i) dans lequel ledit monomère hydrophile à réaction lente comprend un groupe réactif choisi dans le groupe constitué de N-vinylamides, carbamates de O-vinyle, carbonates de O-vinyle, carbamates de N-vinyle, éthers O-vinyliques, O-2-propényle, dans lequel les groupes vinyle ou allyle peuvent en outre être substitués par un groupe méthyle ; et/ou
ii) dans lequel ledit monomère hydrophile à réaction lente comprend au moins un groupe hydrophile choisi dans le groupe constitué d'hydroxyles, amines, éthers, amides, groupes ammonium, acide carboxylique, carbamates et des combinaisons de ceux-ci ; et/ou
iii) dans lequel ledit monomère hydrophile à réaction lente comprend au moins un groupe hydrophile choisi dans le groupe constitué d'hydroxyles, éthers, amides, acide carboxylique et des combinaisons de ceux-ci.

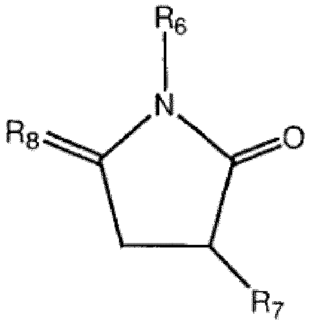
26. Hydrogel de silicone selon la revendication 1 dans lequel ledit monomère hydrophile à réaction lente est choisi parmi un monomère de N-vinylamide de formule I, une vinylpyrrolidone de formule II-IV, une n-vinylpipéridone de formule V :



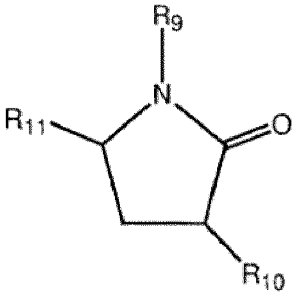
Formule I



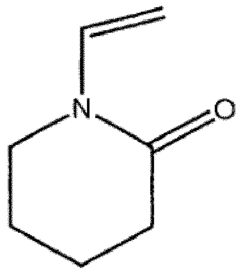
Formule II



Formule III



Formule IV



Formule V

dans lequel R est H ou méthyle ;
R_1, R_2, R_3, R_6, R_7, R_{10} et R_{11} sont indépendamment choisis parmi H, CH_3, CH_2CH_3, $CH_2CH_2CH_3$, $C(CH_3)_2$;
R_4 et R_8 sont indépendamment choisis parmi CH_2, $CHCH_3$ et C (CH_3) ;
R_5 est choisi parmi H, méthyle, éthyle ; et
R_9 est choisi parmi $CH=CH_2$, $CCH_3=CH_2$, et $CH=CHCH_3$.

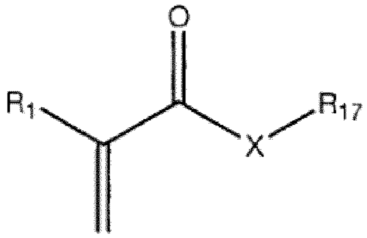
27. Hydrogel de silicone selon la revendication 26 dans lequel :

i) le monomère hydrophile à réaction lente est choisi parmi la vinylpyrrolidone de formule II ou IV ou le monomère de N-vinylamide de formule I, et le nombre total d'atomes de carbone dans R_1 et R_2 est 4 ou moins ; ou
ii) le monomère hydrophile à réaction lente est choisi parmi une vinylpyrrolidone de formule III ou IV et R_6 est méthyle, R_7 est hydrogène, Rg est $CH=CH_2$, R_{10} et R_{11} sont H ; ou
iii) le monomère hydrophile à réaction lente est choisi parmi l'éther vinylique d'éthylène glycol (EGVE), l'éther vinylique de di(éthylène glycol) (DEGVE), la N-vinylpyrrolidone (NVP), la 1-méthyl-3-méthylène-2-pyrrolidone, la 1-méthyl-5-méthylène-2-pyrrolidone, la 5-méthyl-3-méthylène-2-pyrrolidone ; la 1-éthyl-5-méthylène-2-pyrrolidone, la N-méthyl-3-méthylène-2-pyrrolidone, la 5-éthyl-3-méthylène-2-pyrrolidone, la 1-n-propyl-3-méthylène-2-pyrrolidone, la 1-n-propyl-5-méthylène-2-pyrrolidone, la 1-isopropyl-3-méthylène-2-pyrrolidone, la 1-isopropyl-5-méthylène-2-pyrrolidone, le N-vinyl-N-méthyle acétamide (VMA), le N-vinyl-N-éthylacétamide, le N-vinyl-N-éthylformamide, le N-vinylformamide, le N-vinylacétamide, le N-vinylisopropylamide, l'alcool allylique, le N-vinylcaprolactame, le carbamate de N-2-hydroxyéthylvinyle, l'ester N-vinylique de N-carboxy-β-alanine ; la N-carboxyvinyl-β-alanine (VINAL), la N-carboxyvinyl-α-alanine et des mélanges de ceux-ci ; ou
iii) dans lequel le monomère hydrophile à réaction lente est choisi parmi NVP, VMA et la 1-méthyl-5-méthylène-2-pyrrolidone ; ou
iv) dans lequel le monomère hydrophile à réaction lente comprend NVP.

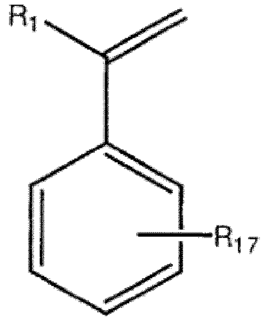
28. Hydrogel de silicone selon la revendication 26 dans lequel ledit composant contenant une silicone comprend au moins un groupe hydroxyle.

29. Hydrogel de silicone selon la revendication 26 comprenant en outre au moins un monomère d'hydroxyalkyle.

30. Hydrogel de silicone selon la revendication 29 dans lequel ledit monomère d'hydroxyalkyle est choisi parmi un monomère de (méth)acrylate ou (méth)acrylamide d'hydroxyalkyle de formule VII ou un composé styryle de formule VIII



FORMULE VII



FORMULE VIII

dans lequel R_1 est H ou méthyle,
X est O ou NR_{16}, R_{16} est H, alkyle en C_1 à C_4, qui peut être en outre substitué par au moins un OH, et
R_{17} est choisi parmi alkyle mono ou dihydroxy-substitué en C_2-C_4, et poly(éthylène glycol) ayant 1 à 10 motifs de répétition.

31. Hydrogel de silicone selon la revendication 30 dans lequel :

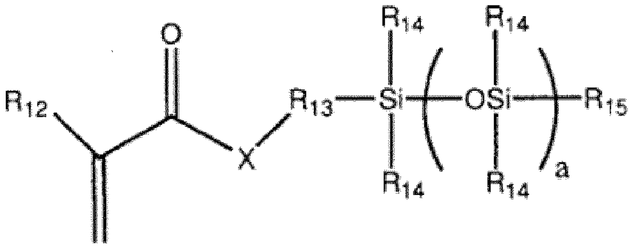
i) R_1 est H ou méthyle, X est oxygène et R est choisi parmi alkyle mono ou dihydroxy-substitué en C_2-C_4, et poly(éthylène glycol) ayant 1 à 10 motifs de répétition ; ou
ii) R_1 est méthyle, X est oxygène et R_{17} est choisi parmi alkyle mono ou dihydroxy-substitué en C_2-C_4, et poly(éthylène glycol) ayant 2 à 20 motifs de répétition.

32. Hydrogel de silicone selon la revendication 29

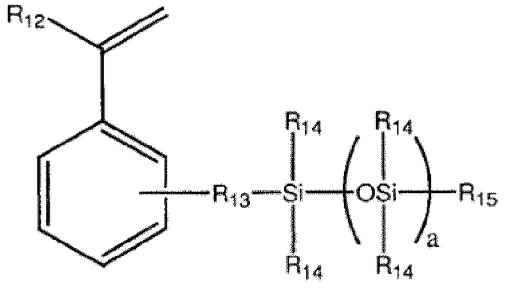
i) dans lequel ledit monomère d'hydroxyalkyle est choisi parmi les méthacrylate de 2-hydroxyéthyle, acrylate de 2-hydroxyéthyle, (méth)acrylate de 3-hydroxypropyle, (méth)acrylate de 2-hydroxypropyle, 2-(méth)acrylate de 1-hydroxypropyle, (méth)acrylate de 2-hydroxy-2-méthyl-propyle, (méth)acrylate de 3-hydroxy-2,2-diméthyl-propyle, (méth)acrylate de 4-hydroxybutyle, (méth)acrylate de glycérol, (méth)acrylamide de 2-hydroxyéthyle, monométhacrylate de polyéthylèneglycol, bis-(2-hydroxyéthyl)(méth)acrylamide, 2,3-dihydroxypropyl(méth)acrylamide, et des mélanges de ceux-ci ; ou
ii) dans lequel ledit monomère d'hydroxyalkyle est choisi dans le groupe constitué des méthacrylate de 2-hydroxyéthyle, méthacrylate de glycérol, méthacrylate de 2-hydroxypropyle, méthacrylate d'hydroxybutyle, méthacrylate de 3-hydroxy-2,2-diméthyl-propyle, et des mélanges de ceux-ci ; ou
iii) dans lequel ledit monomère d'hydroxyalkyle comprend le méthacrylate de 2-hydroxyéthyle, le méthacrylate de 3-hydroxy-2,2-diméthyl-propyle, le méthacrylate de glycérol et des mélanges comprenant ceux-ci.

33. Hydrogel de silicone selon la revendication 1 dans lequel l'au moins un monomère contenant une silicone est monofonctionnel et comprend (a) un groupe réactif choisi parmi des (méth)acrylates, des styryles, des amides et des mélanges de ceux-ci et (b) une chaîne polydialkylsiloxane et peut facultativement contenir du fluor.

34. Hydrogel de silicone selon la revendication 1 dans lequel ledit composant contenant une silicone est choisi parmi un monomère de mono(méth)acryloxyalkylpolydialkylsiloxane de formule IX ou le monomère de styrylpolydialkylsiloxane de formule X :



Formule IX



Formule X

dans lequel R_{12} est H ou méthyle ;
X est O ou NR_{16} ;
chaque R_{14} est indépendamment un alkyle en C_1 à C_4 qui peut être substitué par fluor, ou phényle ;
R_{15} est un alkyle en C_1 à C_4 ;
R_{13} est un groupe alkyle divalent, qui peut en outre être fonctionnalisé avec un groupe choisi dans le groupe constitué de groupes éther, groupes hydroxyle, groupes carbamate et des combinaisons de ceux-ci ;
a est 3 à 50 ;
R_{16} est choisi parmi H, C_{1-4}, qui peut être en outre substitué par un ou plusieurs groupes hydroxyle.

35. Hydrogel de silicone selon la revendication 34 dans lequel ;

i) chaque R_{14} est indépendamment choisi parmi des groupes éthyle et méthyle ; ou
ii) tous les R_{14} sont méthyle.

36. Hydrogel de silicone selon la revendication 34

i) dans lequel R_{12} et chaque R_{14} sont méthyle ; ou
ii) dans lequel au moins un R_{14} est 3,3,3-trifluoropropyle ; ou
iii) dans lequel R_{13} est choisi parmi des groupes alkylène en C_1-C_6 qui peuvent être substitués par éther, hydroxyle et des combinaisons de ceux-ci ; ou
iv) dans lequel R_{13} est choisi parmi des groupes alkylène en C_1 ou C_3-C_6 qui peuvent être substitué par éther, hydroxyle et des combinaisons de ceux-ci ; ou
v) dans lequel a est 5 à 15 ; ou
vi) dans lequel R_{16} est H ou méthyle ; ou
vii) dans lequel ledit méthacrylate de monométhacryloxyalkylpolydiméthylsiloxane est choisi dans le groupe constitué des polydiméthylsiloxane à terminaison monométhacryloxypropyle et à terminaison mono-n-butyle, polydiméthylsiloxane à terminaison monométhacryloxypropyle et à terminaison mono-n-méthyle, polydiéthylsiloxane à terminaison monométhacryloxypropyle et à terminaison mono-n-butyle, polydiéthylsiloxane à terminaison monométhacryloxypropyle et à terminaison mono-n-méthyle, N-(2,3-dihydroxypropane)-N'-(propyltétra(diméthylsiloxy)diméthylbutylsilane)acrylamide, α-(2-hydroxy-1-méthacryloxypropyloxypropyl)-ω-butyloctaméthylpentasiloxane, et des mélanges de ceux-ci ; ou
viii) dans lequel ledit méthacrylate de monométhacryloxyalkylpolydiméthylsiloxane est choisi dans le groupe constitué des polydiméthylsiloxane à terminaison monométhacryloxypropyle et à terminaison mono-n-butyle, polydiméthylsiloxane à terminaison monométhacryloxypropyle et à terminaison mono-n-méthyle, N-(2,3-dihydroxypropane)-N'-(propyltétra(diméthylsiloxy)diméthylbutylsilane)acrylamide, et des mélanges de ceux-ci.

37. Hydrogel de silicone selon l'une quelconque des revendications précédentes comprenant en outre

i) au moins un monomère de réticulation ; et/ou
ii) comprenant en outre au moins un photoamorceur.

38. Hydrogel de silicone selon l'une quelconque des revendications précédentes comprenant en outre un angle de contact montant de :

i) moins de 80° ; ou
ii) moins de 70°.

39. Hydrogel de silicone selon l'une quelconque des revendications précédentes comprenant en outre de 5 à 20 % en poids d'au moins un diluant polaire, sur la base de la totalité des composants dans le mélange de réaction.

40. Hydrogel de silicone selon l'une quelconque des revendications précédentes dans lequel ledit mélange de réaction comprend moins de 5 % de composants hydrophiles à réaction intermédiaire.

41. Hydrogel de silicone selon l'une quelconque des revendications précédentes dépendante de la revendication 8, dans lequel ledit au moins un agent de réticulation à réaction lente et au moins un agent de réticulation à réaction rapide sont chacun présents dans ledit mélange de réaction dans des quantités comprises entre :

i) 0,05 à 0,3 % en poids ; ou
ii) 0,1 à 0,2 % en poids.

42. Hydrogel de silicone selon l'une quelconque des revendications précédentes dépendante de la revendication 8, dans lequel tous les agents de réticulation sont présents en une quantité comprise entre 0,5 % en poids et 2 % en poids.

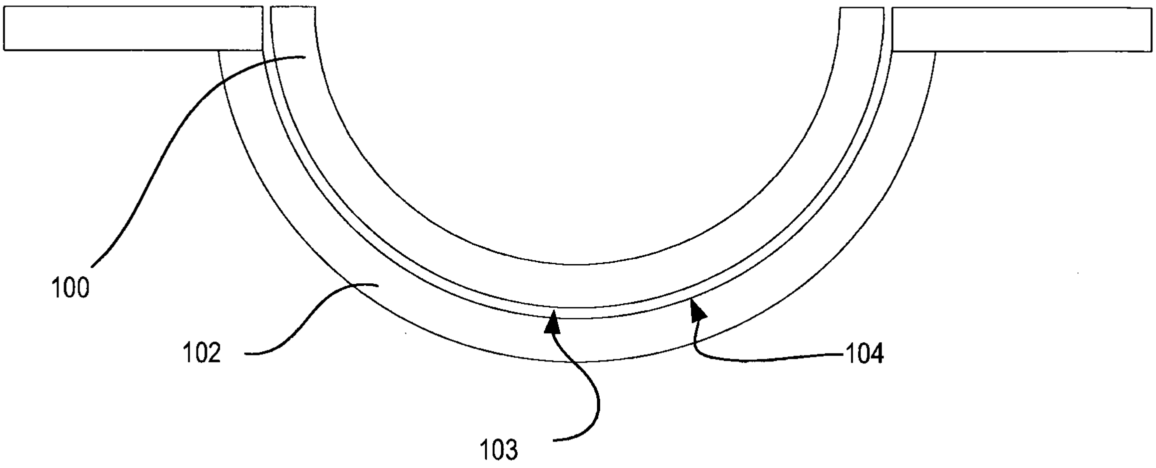


FIG. 1

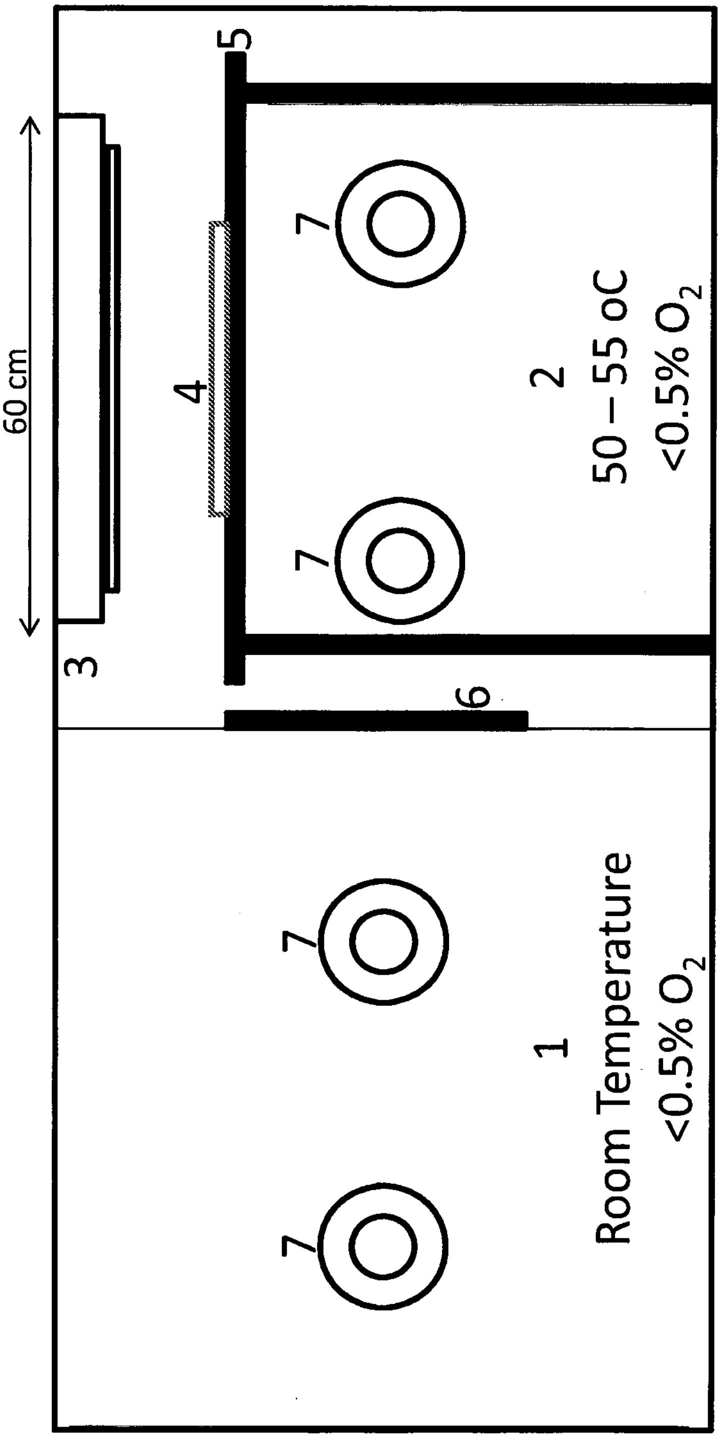


FIG. 2

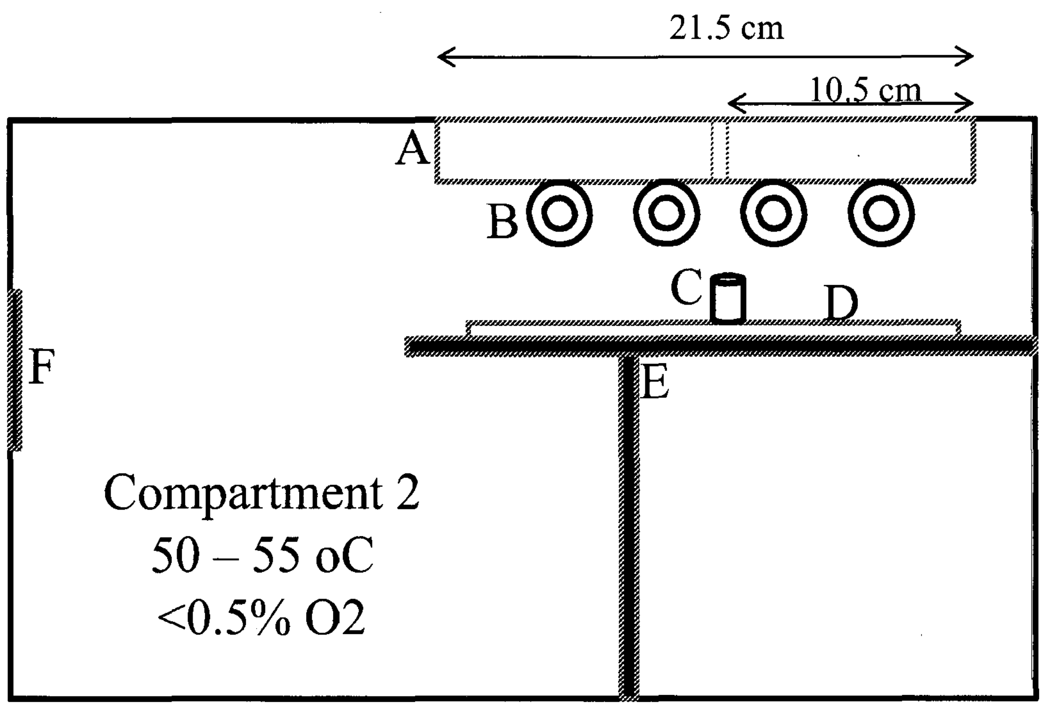


FIG. 3

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